

MATERIALS SCIENCE AND TECHNOLOGIES

# Adhesives

*Types,  
Mechanics and  
Applications*

**Jack S. Doyle ♦ Ryan C. O'Quinn**  
Editors

NOVA



**MATERIALS SCIENCE AND TECHNOLOGIES**

# **ADHESIVES: TYPES, MECHANICS AND APPLICATIONS**

No part of this digital document may be reproduced, stored in a retrieval system or transmitted in any form or by any means. The publisher has taken reasonable care in the preparation of this digital document, but makes no expressed or implied warranty of any kind and assumes no responsibility for any errors or omissions. No liability is assumed for incidental or consequential damages in connection with or arising out of information contained herein. This digital document is sold with the clear understanding that the publisher is not engaged in rendering legal, medical or any other professional services.

# **MATERIALS SCIENCE AND TECHNOLOGIES**

Additional books in this series can be found on Nova's website  
under the Series tab.

Additional E-books in this series can be found on Nova's website  
under the E-books tab.

**MATERIALS SCIENCE AND TECHNOLOGIES**

# **ADHESIVES: TYPES, MECHANICS AND APPLICATIONS**

**JACK S. DOYLE  
AND  
RYAN C. O'QUINN  
EDITORS**



**Nova Science Publishers, Inc.**  
*New York*

Copyright © 2011 by Nova Science Publishers, Inc.

**All rights reserved.** No part of this book may be reproduced, stored in a retrieval system or transmitted in any form or by any means: electronic, electrostatic, magnetic, tape, mechanical photocopying, recording or otherwise without the written permission of the Publisher.

For permission to use material from this book please contact us:

Telephone 631-231-7269; Fax 631-231-8175

Web Site: <http://www.novapublishers.com>

### NOTICE TO THE READER

The Publisher has taken reasonable care in the preparation of this book, but makes no expressed or implied warranty of any kind and assumes no responsibility for any errors or omissions. No liability is assumed for incidental or consequential damages in connection with or arising out of information contained in this book. The Publisher shall not be liable for any special, consequential, or exemplary damages resulting, in whole or in part, from the readers' use of, or reliance upon, this material. Any parts of this book based on government reports are so indicated and copyright is claimed for those parts to the extent applicable to compilations of such works.

Independent verification should be sought for any data, advice or recommendations contained in this book. In addition, no responsibility is assumed by the publisher for any injury and/or damage to persons or property arising from any methods, products, instructions, ideas or otherwise contained in this publication.

This publication is designed to provide accurate and authoritative information with regard to the subject matter covered herein. It is sold with the clear understanding that the Publisher is not engaged in rendering legal or any other professional services. If legal or any other expert assistance is required, the services of a competent person should be sought. FROM A DECLARATION OF PARTICIPANTS JOINTLY ADOPTED BY A COMMITTEE OF THE AMERICAN BAR ASSOCIATION AND A COMMITTEE OF PUBLISHERS.

Additional color graphics may be available in the e-book version of this book.

### Library of Congress Cataloging-in-Publication Data

Adhesives : types, mechanics, and applications / editors, Jack S. Doyle and Ryan C. O'Quinn.

p. cm.

Includes index.

ISBN 978-1-61324-819-5

1. Adhesives. I. Doyle, Jack S. II. O'Quinn, Ryan C.

TA455.A34A345 2011

620.1'99--dc23

2011016432

*Published by Nova Science Publishers, Inc. †New York*

# CONTENTS

|                  |                                                                                                                                                                                                                                      |            |
|------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| <b>Preface</b>   |                                                                                                                                                                                                                                      | <b>vii</b> |
| <b>Chapter 1</b> | Experimental Analysis of the Mechanical Behaviour of a Ductile Adhesive in a Bonded Joint Under Proportional Tensile-Shear Loads<br><i>Jean Yves Cognard, Laurent Sohier, Pierre Jousset, Romain Créac'hcadec and Mohamed Rachik</i> | <b>1</b>   |
| <b>Chapter 2</b> | Pressure-Sensitive Adhesives<br><i>Zbigniew Czech and Agnieszka Kowalczyk</i>                                                                                                                                                        | <b>47</b>  |
| <b>Chapter 3</b> | Electrically Conductive Adhesives Based on Epoxy Resins Reinforced with Carbon Nanofillers<br><i>Silvia G. Prolongo, María R. Gude and Alejandro Ureña</i>                                                                           | <b>71</b>  |
| <b>Chapter 4</b> | Anti-adhesive Layer for Nanoimprint Lithography<br><i>Jing Zhang, Weimin Zhou, Yanbo Liu, Jinhe Wang and Yanping Zhang</i>                                                                                                           | <b>95</b>  |
| <b>Chapter 5</b> | On the Design of Press-Fitted and Adhesively Bonded Joints: Static and Fatigue Tests in Steel and Aluminum Connections<br><i>D. Croccolo, M. De Agostinis and N. Vincenzi</i>                                                        | <b>113</b> |
| <b>Chapter 6</b> | Tissue Adhesives<br><i>Ankit Sarin, Govind Nandkumar and Gregory Dakin</i>                                                                                                                                                           | <b>137</b> |
| <b>Index</b>     |                                                                                                                                                                                                                                      | <b>155</b> |



## PREFACE

In this book, the authors present current research in the study of the types, mechanics and applications of adhesives. Topics discussed include the mechanical behavior of aductile adhesives in bonded joints; pressure-sensitive acrylic adhesives applied in many industrial fields; electrically conductive adhesives; anti-adhesive layers for nanoimprint lithography; the static and fatigue strength of interference fitted connections supplemented with anaerobic adhesives and tissue adhesives as alternatives to traditional sutures and staples.

Chapter 1 – The use of adhesively bonded joints is often limited by a lack of reliable models able to accurately predict the behaviour of industrial bonded parts, in which the stress distribution is often complex. The mechanical behaviour of an adhesive in a bonded joint is often strongly dependent on the stress state (i.e. the tensile-shear combinations) and on the strain rate. Thus, a large experimental database is required to accurately represent the complex behaviour of an adhesive in a bonded joint. On one hand, the yield surface has often to be described taking into account the two stress invariants, the hydrostatic stress and the von Mises equivalent stress, and on the other hand the non-linear behaviour of the adhesive is also quite complex to model. Moreover, the mechanical response of adhesively bonded assemblies often presents large stress concentrations; thus, the analysis of experimental tests can be made particularly difficult. Stress singularities can contribute to crack initiations in the adhesive. Thus, to obtain reliable experimental data, tests which strongly limit the influence of stress singularities must be proposed in order to analyze the non-linear behaviour of an adhesive in a bonded joint. Obtaining reliable experimental results makes it possible to contribute to

optimization of industrial adhesive bonded joints. This chapter presents comparisons between results of different experimental tests (with bulk and bonded assemblies), where some of them are designed to strongly limit the influence of edge effects. Precise finite element computations were used to analyze the stress concentration in the adhesive under elastic assumption. Various experimental results are presented for a ductile adhesive, under proportional tensile-shear loads, using a modified Arcan device. First, the plastic behaviour of the adhesive is analysed using monotonic loads. These experimental results are used to develop a 3D non-associated pressure dependent elasto-plastic model for the adhesive. Then, the influence of the strain rate and the type of load (monotonic, cyclic, relaxation ...) are also presented in order to analyse the viscous effects of such an adhesive.

Chapter 2 – Since their introduction half a century ago, pressure-sensitive acrylic adhesives (PSAs) have been successfully applied in many industrial fields. They are used in self-adhesive tapes, labels and protective films as well as in dermal dosage systems for pharmaceutical applications, in biomedical electrodes, the assembly of automotive parts, toys, and electronic circuits and keyboards. In the last fifty years or so, pressure-sensitive adhesive have made tremendous strides from what was virtually a black art to what is now a sophisticated science. So much so that both the few larger manufacturers of pressure-sensitive adhesive articles and their even larger suppliers now use very expensive equipment to study pressure-sensitive adhesive behavior: tack, adhesion and cohesion.

Chapter 3 – The present chapter is a review of the most relevant experimental results obtained for the development of conductive nanoreinforced adhesives. The epoxy adhesives are filled with low loadings of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) in order to increase widely their electrical conductivity, remaining their adhesive ability and even improving their mechanical and thermal behaviour. Taking into account their possible applications as structural adhesives, the adhesive strength and toughness of the joints was measured using lightweight adherends, as carbon fiber/epoxy laminates, which are commonly used in the aerospace and automobile industries.

The critical stage of the manufacturing process of nanoreinforced adhesives is the dispersion of the nanofillers. A dispersion procedure based on the use of an organic solvent was optimised to reach suitable dispersion degrees at low carbon nanofiller contents ( $< 0.5$  wt.%). High nanofiller concentrations had to be rejected due to the excessive increase of the adhesive viscosity.

The addition of CNFs and CNTs was probed to induce a light increase of the maximum use temperature of the adhesive and an important improvement of their tensile mechanical properties. The lap shear strength is not affected by the presence of the nanofillers while the joint toughness, measured by double cantilever beam test, significantly increases. It was probed that both properties strongly depend on the surface pre-treatment applied to the laminate adherends. Also, nanoreinforced epoxy adhesives show high electrical conductivity, allowing the dissipation of electrostatic charges when conductive adherends are joined.

Chapter 4 – Nanoimprint lithography is a method of fabricating nano-scale patterns with low cost, high throughput and high resolution. However, during nanoimprint lithography process, adhesion between the resist and the mold is one of the very factors which has affected the imprinted nanopatterns. As a result, improving anti-sticking properties of the stamps for nanoimprint lithography was intensively developed. In this chapter, the history and fabrication methods of anti-adhesive layer are reviewed in detail. Especially, we had developed a novel method of anti-adhesively self-assembled film by vapor phase deposition. Finally, personal remark is briefly ended with some views on the development of anti-adhesive layers.

Chapter 5 – The work is focused on the static and fatigue strength of interference fitted connections supplemented with anaerobic adhesive (*Hybrid Joints*). Through axial release tests it is demonstrated that the addition of the adhesive always improves the performance of the joint: the main achievable benefits can be summarized in (i) the possibility of increasing the load transfer capability with the same joint geometry and (ii) reducing both the weight and the stress field of the joint with the same load transfer capability. The aim of the work is to provide some relevant information on the static and fatigue strength properties in case of both steel-aluminium components (*Mixed Hybrid Joints*) and steel-steel components (*Steel Hybrid Joints*). Proposed results derive from a collection of 200 experimental tests performed by the Authors on a high strength, single-component adhesive, which cures anaerobically (Loctite 648®).

Chapter 6 – The medical community has continually sought an efficient method of wound closure that requires little time and minimizes discomfort for patients, yet produces a good cosmetic outcome. Over the last few decades tissue adhesives have emerged as alternatives to traditional sutures and staples. These biological and synthetic compounds have the advantage of ease of use, excellent results, and high patient acceptability. In fact, the uses of these tissue adhesives have gradually evolved beyond wound closure to include a variety

of medical applications as diverse as the treatment of cerebral arteriovenous malformations to the control of gastrointestinal bleeding. Tissue adhesives are an area of active research, with novel applications continuing to emerge.

This chapter summarizes the major types of adhesives available, tracing the history of development, and highlighting the unique properties of each of the five major compounds available: Cyanoacrylates, Albumin based compounds, Fibrin based & Collagen based adhesives, and Polyethylene Glycol Polymers. We also review the medical applications of these compounds as well as provide an overview of the major brands available in the US. We conclude with a brief discussion of the newer areas of research as well as emerging applications.

## *Chapter 1*

# **EXPERIMENTAL ANALYSIS OF THE MECHANICAL BEHAVIOUR OF A DUCTILE ADHESIVE IN A BONDED JOINT UNDER PROPORTIONAL TENSILE-SHEAR LOADS**

***Jean Yves Cognard<sup>1\*</sup>, Laurent Sohier<sup>2</sup>, Pierre Jousset<sup>3</sup>,  
Romain Créac'hcadec<sup>1</sup> and Mohamed Rachik<sup>4</sup>***

<sup>1</sup>Laboratoire Brestois de Mécanique et des Systèmes, ENSTA Bretagne,  
Université de Brest, ENIB, Université Européenne de Bretagne,  
ENSTA Bretagne, 2 rue F. Verny, 29806 Brest, France

<sup>2</sup>Laboratoire Brestois de Mécanique et des Systèmes, Université de Brest,  
6 Av. Le Gorgeu, 29285 Brest, France

<sup>3</sup>Sika Technology AG, Tüffenwies 16, 8048 Zürich, Switzerland

<sup>4</sup>Laboratoire LRM, Université de Technologie de Compiègne,  
60205 Compiègne, France

## **ABSTRACT**

The use of adhesively bonded joints is often limited by a lack of reliable models able to accurately predict the behaviour of industrial bonded parts, in which the stress distribution is often complex. The mechanical behaviour of an adhesive in a bonded joint is often strongly dependent on the stress state (i.e. the tensile-shear combinations) and on the strain rate. Thus, a large

experimental database is required to accurately represent the complex behaviour of an adhesive in a bonded joint. On one hand, the yield surface has often to be described taking into account the two stress invariants, the hydrostatic stress and the von Mises equivalent stress, and on the other hand the non-linear behaviour of the adhesive is also quite complex to model. Moreover, the mechanical response of adhesively bonded assemblies often presents large stress concentrations; thus, the analysis of experimental tests can be made particularly difficult. Stress singularities can contribute to crack initiations in the adhesive. Thus, to obtain reliable experimental data, tests which strongly limit the influence of stress singularities must be proposed in order to analyze the non-linear behaviour of an adhesive in a bonded joint. Obtaining reliable experimental results makes it possible to contribute to optimization of industrial adhesive bonded joints. This chapter presents comparisons between results of different experimental tests (with bulk and bonded assemblies), where some of them are designed to strongly limit the influence of edge effects. Precise finite element computations were used to analyze the stress concentration in the adhesive under elastic assumption. Various experimental results are presented for a ductile adhesive, under proportional tensile-shear loads, using a modified Arcan device. First, the plastic behaviour of the adhesive is analysed using monotonic loads. These experimental results are used to develop a 3D non-associated pressure dependent elasto-plastic model for the adhesive. Then, the influence of the strain rate and the type of load (monotonic, cyclic, relaxation ...) are also presented in order to analyse the viscous effects of such an adhesive.

**Keywords:** Adhesive testing, Joint design, Stress analysis, Edge effects, Non-linear behaviour, Non-associated pressure dependent elasto-plastic model.

## INTRODUCTION

Adhesively bonded assemblies can simplify the design and reduce the cost and the weight of structures with respect to riveting or bolt joining (Kinloch 1987, [1], Adams 2005, [2]; da Silva et al. 2008, [3]). Despite various advantages, especially when assembling dissimilar materials or composite materials, the use of adhesive bonding is not yet widespread as a lack of confidence still exists. In fact, the stress state in a bonded joint can be complex, as bonded assemblies are often characterised by large stress concentrations which, in particular, make the analysis of experimental tests difficult (Leguillon and Sanchez-Palencia 1987, [4]; Wang and Rose 2000, [5]). Thus, reliable experimental data are required to develop numerical tools in order to accurately predict the mechanical behaviour of industrial bonded assemblies. On the one hand, the yield surface (elastic limit)

often has to be described taking into account the two stress invariants, the hydrostatic stress and the von Mises equivalent stress (Raghava et al. 1973, [6]; Mahnken and Schlimmer 2005, [7]), and on the other hand the non-linear behaviour of the adhesive is also quite complex to model (Rolfes et al. 2008, [8]; Créac'hédec and Cognard 2009, [9]). Moreover, for industrial applications, the failure envelope of the adhesive should also be precisely determined for different types of loadings (monotonic, cyclic, non-proportional...). One has to take into account the influence of various parameters such as the possible complex non-linear behaviour of the adhesive, the geometry of the different parts, the joint thickness, the stress state (i.e. the tensile-shear combinations) and the strain rate...

Basically, experimental tests can be divided into two main categories: tests on bulk specimens and tests in a joint or in-situ (Dolev and Ishai 1981, [10]; Jeandreau 1991, [11]). Tests in the bulk form are quite easy to perform and follow the standards for plastic materials. But it has been shown that bulk specimens and bonded joints have different mechanical properties especially close to failure (Jeandreau 1991, [11]; Montois et al. 2007, [12]; Lilleheden 1994, [13]; da Silva and Adams 2005, [14]). Curing conditions may be different in the bulk form and in a joint (thin film) due to the adhesive thickness and to the substrates which can remove the heat produced by the exothermic curing reaction and prevent overheating. Moreover, in a joint, interfaces strongly constrain the adhesive, preventing deformation along it and creating areas called interphases where a gradient of mechanical property exists. In addition, the interphases properties are quite different from those of the bulk material (Montois et al. 2007, [12]; Bouchet et al. 1999, [15]). For instance, in bulk tension, a small void will cause a premature failure whereas in the thick adherend shear test (TAST), the presence of a void is not as critical. In-situ tests are more representative of industrial applications, but for usual tests there are some difficulties associated with stress concentrations (Deal et al. 2004, [16]; Cognard et al. 2008, [17]).

The single-lap joint is the most used test to analyse the behaviour of an adhesive in bonded joint, mainly under shear load. But large peel stresses develop at the two ends of the overlap in such specimens. Moreover, significant stress concentrations, which are associated with geometrical and material parameters, can be observed. Thus, peel and cleavage forces, in particular, make the analysis of experimental results difficult, and can limit the load transmitted by the bonded joint despite various techniques proposed to limit the influence of edge effects (Adams and Harris 1987, [18]; Hildebrand 1987, [19]; Belingardi et al. 2002, [20]). The stress singularities can contribute to fracture initiation in the adhesive and thus leading to an incorrect analysis of the behaviour of the adhesive (Dean et al. 2004, [16]; Cognard et al. 2008, [17]). With such single-lap shear specimens

the substrate thickness and the overlap length strongly affect the stress concentrations close to the free edges of the adhesive; however, it is very difficult to limit the influence of edge effects to a large extent (Lang and Mallick 1999, [21]). The thick adherend shear test, TAST (ASTM 1996, [22]; Althof 1982, [23]; da Silva and Adams 2005, [14]), simplify the stress distributions in the adhesive. Therefore, this test can be seen as optimized simple-lap shear configuration, but edge effects still exist and can initiate cracks close to the substrate-adhesive interfaces (Kadioglu et al. 2002, [24]; Dean et al. 2004, [16]; Cognard et al. 2008, [17]).

Experimental results under compression/tensile-shear loads are necessary to develop accurate numerical models for the mechanical behaviour of an adhesive in a bonded joint. Different tests exist in the literature for such loads: tension-torsion tests with tubular specimens (Chai 2004, [25]; Mahnken and Schlimmer 2005, [7]), scarf joints (Gacoin et al. 2009, [26]) or the Arcan fixture (Arcan et al. 1987, [27]). However, for various tests, quite an extensive scatter in the results is observed which is associated with the influence of edge effects and with the possible sensitivity to misalignments and defects. Thus, it is useful to design experimental fixtures which strongly limit the influence of edge effects in order to obtain reliable data. Failure initiation in an adhesive between two metallic structures always starts at stress concentration points. Therefore, understanding of the stress state in an adhesive joint can lead to improvements in adhesively-bonded assemblies (Cognard 2008, [28]; Cognard et al. 2010, [29]). This is particularly true because it can be hard to take the effects of stress singularities into account when analyzing experimental results.

The chapter begins by presenting the influence of some parameters on stress distribution in adhesive in the case of the usual single-lap shear specimens. Precise finite element computations were used to analyze the stress state and the stress concentration in the adhesive under elastic assumption. Using results of asymptotic analysis, some properties are presented in order to strongly limit the influence of edge effects. Secondly, using a ductile adhesive, some results of tensile test on bulk specimens and of single-lap shear tests are presented. Moreover, the possibilities of an improved shear test (modified TAST) are presented; this setup, which strongly limits the influence of edge effects, limits the scatter in the experimental results. Then, results under shear-tensile proportional monotonic loadings obtained with a modified Arcan device, which also has been designed to greatly limit the influence of edge effects, are presented. These experimental results are used to fit the material parameters of a 3D non-associated elasto-plastic model for the adhesive, taking into account the influence of the hydrostatic pressure. The last part analyses the influence of different parameters

on the mechanical behaviour of the adhesive; particularly, different types of loads are used in order to characterize the viscous effects of such an adhesive.

The experimental results which follow, unless stated otherwise, were realized using steel substrates, an adhesive thickness of 0.3 mm and a displacement rate of the crosshead of the tensile testing machine of 0.5 mm/min. The ductile structural adhesive SikaPower-470/7 was used for the different experimental tests presented in this chapter. The finite element simulations presented in this paper, unless stated otherwise, were done with the code CAST3M [30] (CEA, Saclay, France).

## ANALYSE OF SINGLE LAP SHEAR SPECIMENS

Several studies have shown that stress singularities for bi-material joints mainly depend on the geometry of the substrates and on the relative elastic properties of the materials, in the case of elastic behaviour. This section presents the influence of some parameters on stress distribution in the adhesive in the case of the usual single-lap shear specimens. Numerical results are presented for adhesive elastic parameters (Young modulus and Poisson's ratio) close to those of adhesive SikaPower-470/7 which is used for the experimental tests. It is important to notice that similar results are obtained for adhesives with similar elastic parameters.

### Influence of Edge Effects for a Lap Shear Specimen

In order to determine the way the stress evolves through the thickness of the adhesive joint, precise finite element analyses have to be performed, assuming a linear elastic behaviour of the components. Since multi-material structures were being modelled, compliance with the mechanical properties of perfect interfaces was necessary. With the standard finite element method, based on the variational principal of minimum potential energy whose single variable is the displacement field, the continuity of the displacement field is satisfied but the continuity of the stress vector is not exactly verified. Therefore, refined meshes are also needed near the interface in order to obtain good numerical results especially for large material heterogeneity of the assemblies (Cheikh et al. 2001, [30]; Goncalves et al. 2002, [16]). Various simulations have shown that good numerical results are obtained using meshes with 20 linear rectangular elements for a 0.1mm thickness of adhesive (Cognard 2008, [28]). Computations were made in 2D (plane stresses) on half of the specimen by applying adequate boundary conditions. Results are

presented for steel substrates (Young modulus:  $E_s = 220$  GPa, Poisson's ratio:  $\nu_s = 0.3$ ) and for aluminium substrates ( $E_a = 80$  GPa,  $\nu_a = 0.3$ ); the material parameters for the adhesive joint are:  $E_j = 2.2$  GPa,  $\nu_j = 0.3$ .

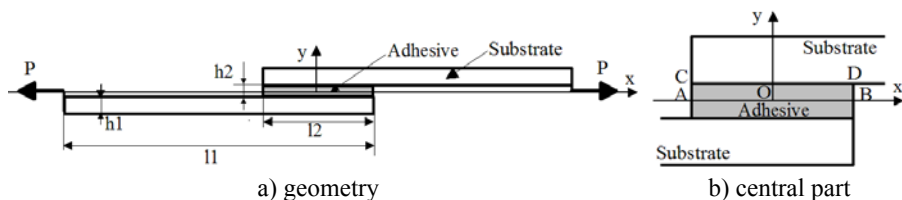


Figure 1. Presentation of the single lap-shear joint.

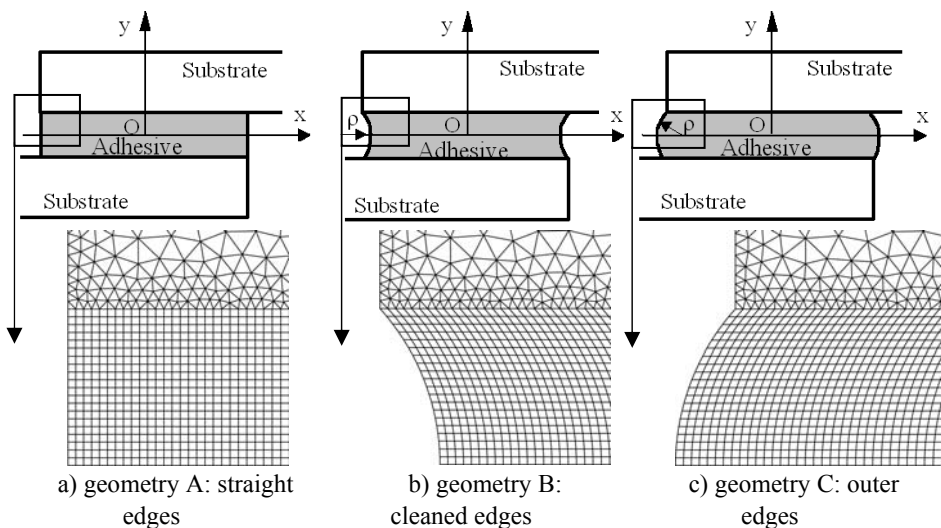


Figure 2. Presentation of geometries A, B and C & mesh for  $h_2 = 0.2$  mm (close-up view).

The parameters which define the geometry of the single lap shear specimen are presented in Figures 1 and 2. The substrate length and the overlap length are denoted by  $l_1$  ( $l_1 = 100$  mm) and  $l_2$ . The substrate and adhesive thicknesses are denoted by  $h_1$  and  $h_2$ . "O" represents the centre of the adhesive (Figure 1b).

A limitation of the influence of edge effects can lead to an increase in the load which can be transmitted by the assembly. In order to briefly present the influence of edge effects on the stress distribution in the adhesive, three geometries of the free edges of the adhesive are used in order to emphasize the influence of the geometry of the adhesive's free edge defined by the radius  $\rho$ , Figure 2, (geometry

A: straight edges,  $\rho = \infty$ ; geometry B: cleaned edges,  $\rho = 0.75 h_2$ ; and geometry C: outer edges,  $\rho = -0.75 h_2$ ;  $h_2$  being the joint thickness).

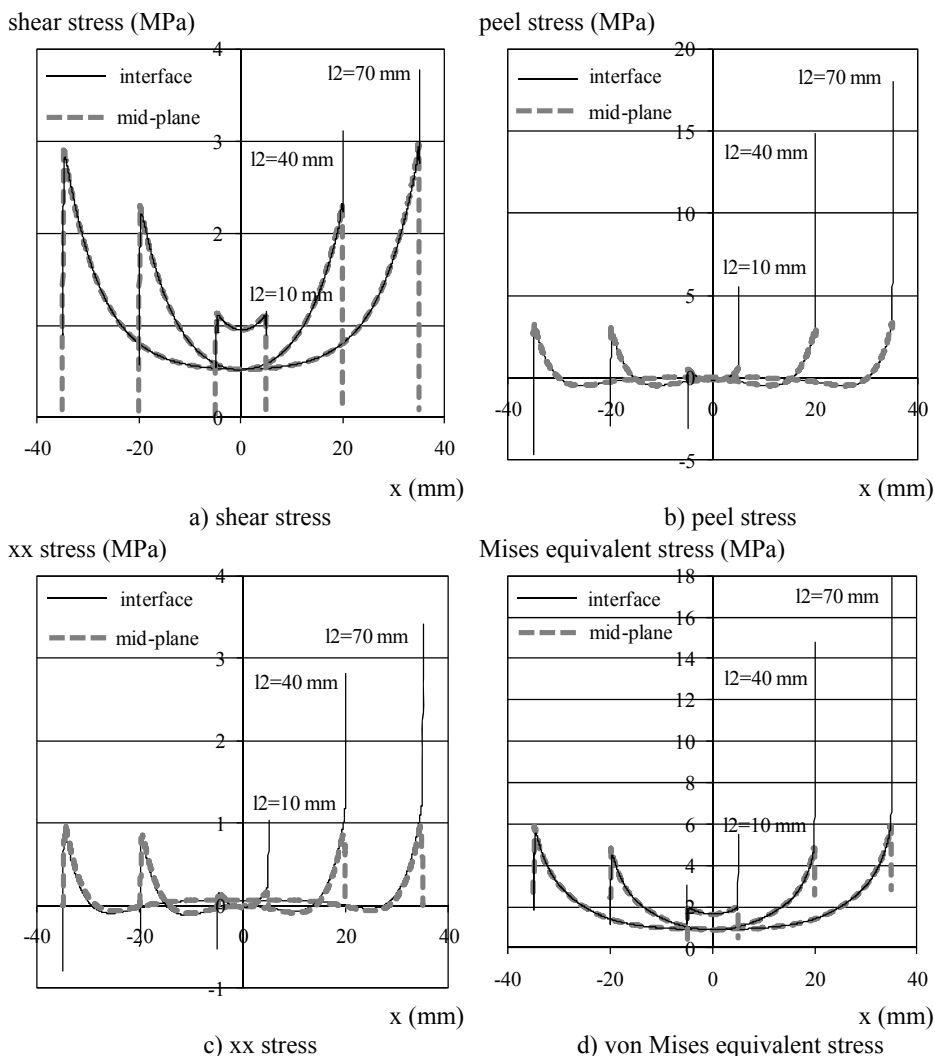


Figure 3. Distribution of the stresses in the adhesive (mid-plane and adhesive-substrate interface) along the overlap length for geometry A, for an average shear stress of 1 MPa, for a substrate thickness of  $h_1 = 6$  mm and for a joint thickness of  $h_2 = 0.3$  mm.

Moreover those examples are used to underline the influence of the overlap length and the substrate rigidity on the stress distribution throughout the adhesive.

Figure 2 also shows the mesh of the adhesive close to the free edges and the mesh of the substrate close to the substrate-adhesive interface in order to respect the properties previously presented.

Figure 2 presents a part of the mesh associated with an adhesive thickness of  $h_2 = 0.2$  mm (only half of the adhesive is modelled). To facilitate the analysis of the numerical results, adhesive is meshed with rectangular elements, thus the distribution of the stresses throughout the thickness of the adhesive can easily be analysed. In order to limit the number of elements, in the model in the middle of the overlap length, the element size can be increased in the  $x$  direction (Figure 2) without influencing the numerical results. Moreover it can be seen that the substrate is meshed using triangular elements which allow the element size in the substrate to be increased quickly in order to limit the finite element model size.

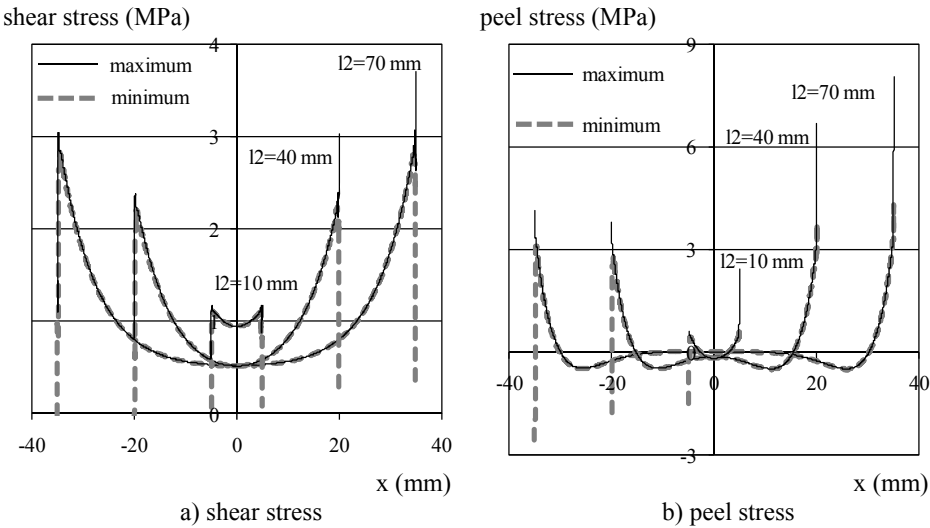


Figure 4. Minimum and maximum values of the stresses through the thickness of the adhesive along the overlap length for geometry B, for an average shear stress of 1 MPa, for a substrate thickness of  $h_1 = 6$  mm and for a joint thickness of  $h_2 = 0.3$  mm.

Figure 3 presents results for geometry A with a joint thickness of  $h_2 = 0.3$  mm, for steel substrates with a thickness of  $h_1 = 6$  mm and for different overlap lengths ( $l_2 = 10, 40$  and  $70$  mm). In order to analyze the stress distribution in the adhesive, results are presented along the mid-plane of the adhesive [A B] ( $y = 0$ , Figure 1b), along the adhesive-substrate interface [C D] ( $y = h_2/2$ , Figure 1b). For those drawings, the average shear stress in the adhesive is normalised to 1, in order to make analysis of the stress distributions easier. Figure 3 presents the

different components of the stress denoted by: “xx”, “yy” (peel stress), “xy” (shear stress). It is important to notice that the stress distribution is not constant in the x direction (even for the shear stress) and that there are quite large edge effects close to point C and D (Figure 1).

**Table 1. Maximum transmitted load by the assembly, for geometry A, a substrate thickness of  $h_1 = 6$  mm and a joint thickness of  $h_2 = 0.3$  mm.**

|                         |       |       |       |
|-------------------------|-------|-------|-------|
| Overlap length: $l_2$   | 10 mm | 40 mm | 70 mm |
| $P_l / P_l=10\text{mm}$ | 1.00  | 1.48  | 2.14  |

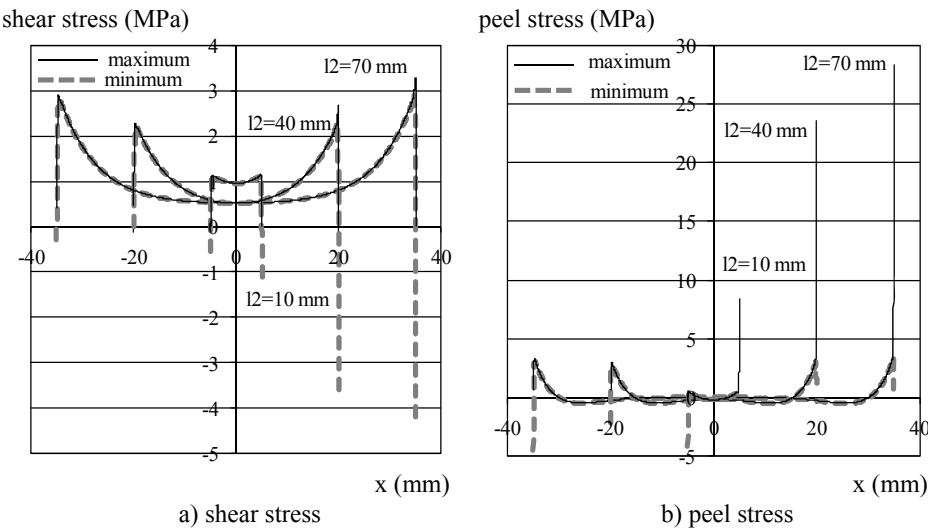
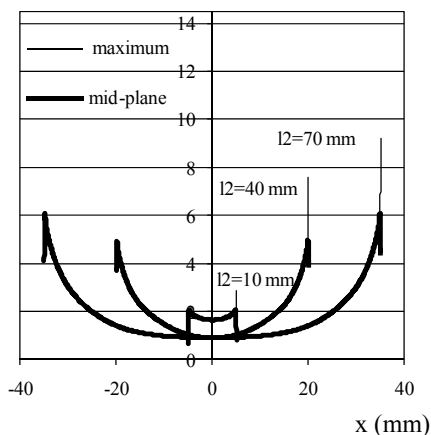


Figure 5. Minimum and maximum values of the stresses through the thickness of the adhesive along the overlap length for geometry C, for an average shear stress of 1 MPa, for a steel substrate thickness of  $h_1 = 6$  mm and for a joint thickness of  $h_2 = 0.3$  mm.

The edge effects are mainly observed on the peel stress. Moreover, for this geometry, the maximum von Mises equivalent stress in the adhesive is obtained at the adhesive-substrate interface which is often the weakest part of the assembly, due either to defects on the surface or to local variations in chemistry (Bouchet et al. 1999, [15]). For the geometry used, an increase of the overlap length increases the stress concentration. Thus using a dimensioning criteria associated with the von Mises equivalent stress, it can be noted that the maximum transmitted load by

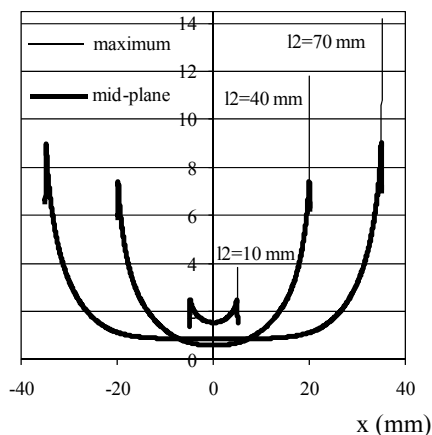
the assembly,  $P_j$  increases slowly with the overlap length (Table 1) and that the maximum average shear stress decreases with the overlap length.

Mises equivalent stress (MPa)



a) steel substrates

Mises equivalent stress (MPa)



b) aluminium substrates

Figure 6. Maximum values of the von Mises equivalent stress through the thickness of the adhesive and distribution of the von Mises equivalent stress in the mid-plane of the joint along the overlap length for geometry B, for an average shear stress of 1 MPa, for a substrate thickness of  $h_1 = 6$  mm and for a joint thickness of  $h_2 = 0.3$  mm.

Figures 4 and 5 present an idea of the stress distribution through the adhesive thickness for geometries B and C (Figure 2). As for such geometries the maximum stress state can be obtained within the joint thickness, for a given abscissa  $x$ , only the minimum and maximum values of the studied quantity are drawn in order to make the analysis of the stress distributions easier. The geometry B (cleaned edges) allows extensive limitation of the influence of edge effects with respect to straight edges (peel stress). However, geometry C leads to quite large stress concentrations.

Figure 6 presents the influence of the mechanical properties of the substrate on the distribution of the maximum of the von Mises equivalent stress through the joint thickness; results are presented for steel and aluminium substrates and it can be seen that for single-lap shear specimens, an increase of the Young modulus of the substrates leads to a reduction of the edge effects associated to an increase of the rigidity of the substrates. Classical analysis of edge effects show that edge effects increase with relative elastic properties of the material (adhesive and substrate), but there is also an influence of the global properties of the studied

structure on the stress concentrations. Figure 6 presents the distribution of the von Mises equivalent stress in the mid-plane of the joint along the overlap length for both aluminium and steel substrates. It can be seen that the stress state in the mid-plane of the joint is not representative of the maximum stress in the joint, associated with the influence of edge effects. Thus, it seems difficult to analyze results of single lap shear tests only taking into account simplified methods which mainly only take into account the average shear stress in the adhesive (da Silva et al. 2009, [33]). Moreover, it has been shown that a significant variation of the stress can exist throughout the thickness of the adhesive; therefore, simplified methods which roughly analyse the average stress state through the joint can overestimate the maximal load transmitted through the single lap joints. Thus, refined analyses of the stress distribution in the adhesive are necessary to obtain precise dimensioning of adhesively-bonded assemblies.

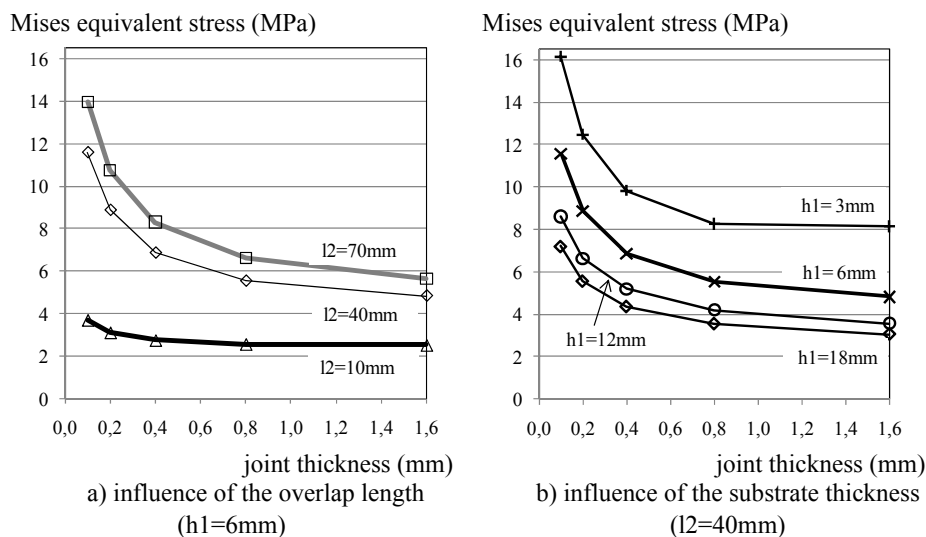


Figure 7. Maximum value of the von Mises equivalent stress in the adhesive with respect to the joint thickness for geometry B and for an average shear stress of 1 MPa.

Results presented in Figure 7 underline that, for single lap-shear specimens an increase of the joint thickness and an increase of the substrate thickness lead to a reduction of the stress concentration in the adhesive under elastic assumption.

## Influence of Different Local Geometries

Numerous studies have been proposed to reduce the stress concentrations in the case of lap joints (Adams and Harris 1987, [18]; Hildebrand 1987, [19]), such as effects of spew and chamfer size (Belingardi et al. 2002, [22]), influence of slots (Yan et al. 2007, [34]).

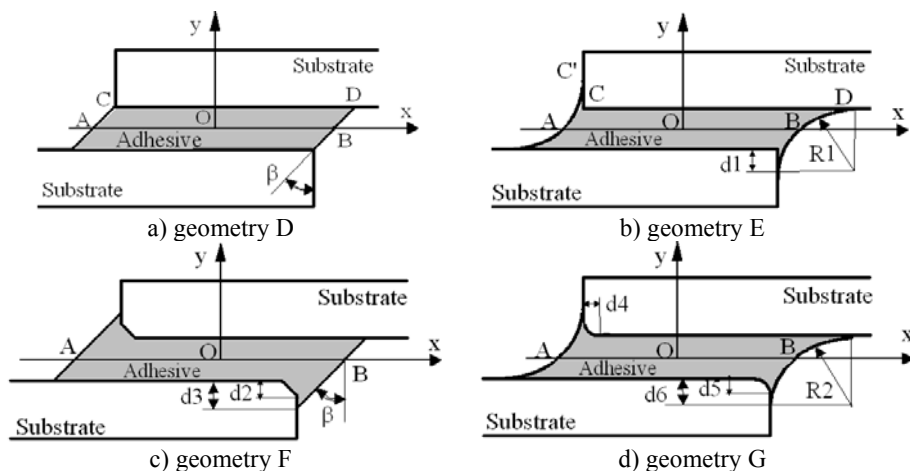
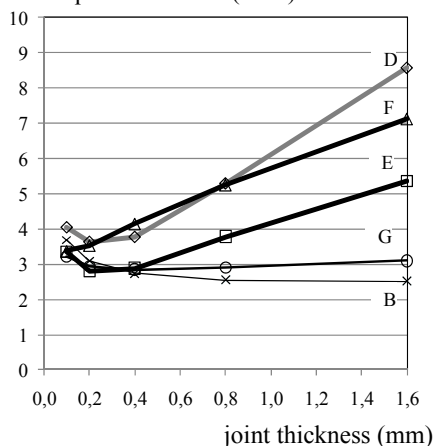


Figure 8. Presentation of geometries D, E, F and G.

Figure 8 presents four geometries (denoted by D, E, F and G) used in various studies in order to limit the influence of edge effects. Geometry D is defined by an angle  $\beta = 45^\circ$ . Geometry E is defined with the following two parameters:  $d1 = h2/2$  and  $R1 = 1.5 h2$ ;  $h2$  being the adhesive thickness. For the geometry F, the main parameters are:  $d2 = h2/2$ ,  $d3 = h2$ ,  $\beta = 45^\circ$  and linear chamfers. Geometry G is defined with:  $d4 = d5 = h2/2$ ,  $d6 = 1.5 h2$ ,  $R2 = 2 h2$  and circular chamfers.

For geometries B, D, E, F and G, the influence of the adhesive thickness on the maximum value of the von Mises equivalent stress, for an average shear stress of 1 MPa, is presented for two overlap lengths (10 and 70 mm) in Figure 9. It can be noted that for an overlap length of 70 mm the geometries E and G give good results; for thick joints geometries B, E and G give similar results. Geometries B, E and G give also nearly similar results for thin joints and for an overlap length of 10 mm. Geometries D and E are associated with quite significant edge effects.

Mises equivalent stress (MPa)

a) overlap length of  $l_2 = 10$  mm

Mises equivalent stress (MPa)

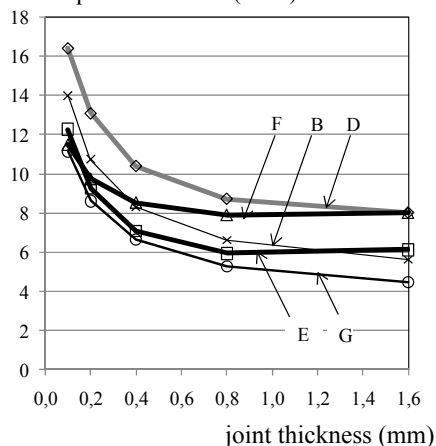
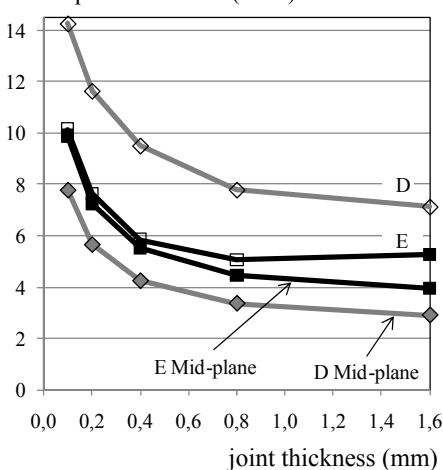
b) overlap length of  $l_2 = 70$  mm

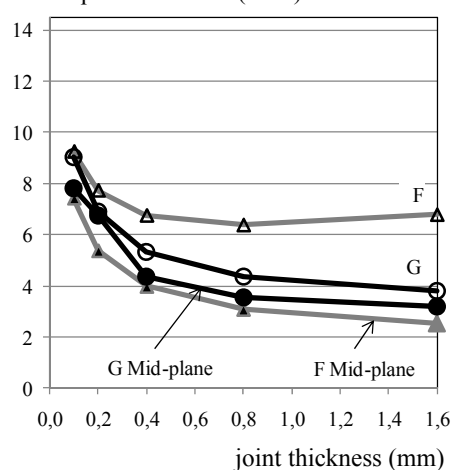
Figure 9. Maximum value of the von Mises equivalent stress in the adhesive for geometries B, D, E, F and G with respect to the joint thickness, for a substrate thickness of  $h_1 = 6$  mm and for an average shear stress of 1 MPa.

Mises equivalent stress (MPa)



a) geometries D &amp; E

Mises equivalent stress (MPa)



b) geometries F &amp; G

Figure 10. Maximum value of the von Mises equivalent stress in the adhesive for geometries D, E, F and G, and of the von Mises equivalent stress in the mid-plane of the joint with respect to the joint thickness, for a substrate thickness of  $h_1 = 6$  mm, for an overlap length of  $l_2 = 40$  mm and for an average shear stress of 1 MPa.

Figure 10 presents the influence of the local geometries of both substrate and adhesive (D, E, F and G) on the maximum of the von Mises equivalent stress through the joint thickness and in the adhesive mid-plane for an average shear stress of 1 MPa. It can be seen that the stress state in the mid-plane of the joint is not representative of the maximum stress in the joint. A reduction of the stress concentration leads to limitation of the stress state in the joint and in the mid-plane of the adhesive. Geometries E and G give good results but as such geometries are not easy to manufacture, larger stress concentrations can be obtained in applications.

## Results of Asymptotic Analysis

Failure initiation in an adhesive joint between two metallic structures always starts at stress concentration points which are often associated with stress singularities. For instance, using asymptotic analysis (Leguillon and Sanchez-Palancia 1987, [4]; Reedy and Guess 1993, [35]; Leguillon et al. 2003, [36]; Cognard et al. 2010, [37]), in the case of 2D problems, under elasticity assumption and close to a corner, the relevant parts of the displacement field  $\mathbf{u}$  and the stress tensor  $\boldsymbol{\sigma}$ , using the polar coordinates  $(r, \theta)$  are given by:

$$\mathbf{u}(r, \theta) \approx k r^\lambda \underline{\mathbf{u}}(\theta) \quad (1)$$

$$\boldsymbol{\sigma}(r, \theta) \approx k r^{\lambda-1} \underline{\boldsymbol{\sigma}}(\theta) \quad (2)$$

The singularity exponent  $\lambda$  is the solution of an eigenvalue problem defined by the boundary closed to the singular point; thus, this parameter depends on the geometry close to the singular point. The intensity factor  $k$  of the problem depends on the complete geometry of the structure and on the external loads.

Computations have been made under 2D hypothesis to analyse the influence of the local geometry close to the substrate-adhesive interface, close to the free edges of the adhesive (Figure 11a). Close to a corner, the geometry of the substrate and of the adhesive can be defined using two angles  $\delta_s$  and  $\delta_a$  (Figure 11a). Figure 11b presents results for steel substrates under plane stress assumptions: it can be seen that in order to obtain a regular solution, it is necessary to decrease the substrate angle  $\delta$  to obtain a quite large admissible adhesive angle  $\delta_a$ . For instance, for  $\delta_s = 90^\circ$ , one has to verify  $\delta_a < 55^\circ$  in order to prevent stress concentrations; therefore, sharp beaks and a cleaning of the

adhesive free edges are useful in order to limit the influence of edge effect (Cognard 2008, [28]; Cognard and Créac'hcadec 2009, [38]; Cognard et al. 2010, [29]). These results give some interesting rules in order to design bonded specimens which significantly limit the influence of edge effects.

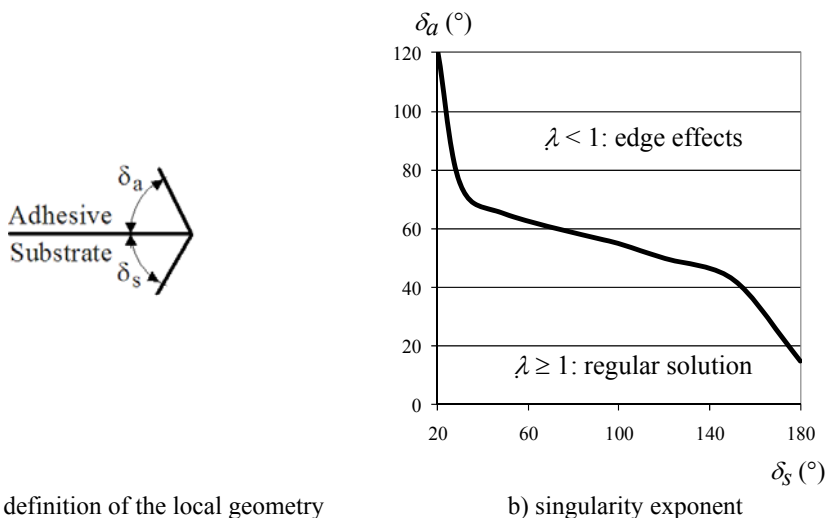


Figure 11. Influence of the local geometry close to a free edge of a substrate-adhesive interface on the singularity exponent  $\lambda$  for bi-material applications with steel substrates.

## Remarks

The previous numerical results underlined that the experimental analyse of the properties of an adhesive in a bonded joint is made difficult by the stress singularities due to edge effects. Stress singularities can contribute to crack initiations in the adhesive (Deal et al. 2004, [16]; Cognard et al. 2008, [17]). Thus, with the single lap-shear test it seems difficult to obtain reliable information about the behaviour of an adhesive in a bonded joint, but it can be used to compare the behaviours of adhesives joints under a complex loading. As the stress state in the adhesive in a bonded joint is quite complex and strongly depends on the local geometry of both adhesive and substrate close to the free edges of the joint, it seems difficult to analyze the stresses in a single-lap tests only taking into account simplified methods which mainly consider the average shear stress in the adhesive (da Silva et al. 2009, [33]). Moreover, it has been shown that the plastic non-linear behaviour of the adhesive joint does not seem to limit the influence of the edge

effects (Cognard et al. 2008, [17]) thus, the lower the equivalent stress (computed under linear elasticity), the lower the risk will be of first rupture near the edge of the joint. Therefore, it is useful to design experimental fixtures which strongly limit the edge effects in order to obtain reliable data (Cognard 2008, [28]; Cognard et al. 2010, [29]).

## PRESENTATION OF THE STRUCTURAL ADHESIVE SIKAPOWER-490/7

### Adhesives and Substrates

The structural adhesive SikaPower-490/7 (Sika 2009, [39]) was used for the different experimental results presented in this chapter. It is a one component body-in-white hot-curing adhesive optimised for automotive applications. It can be applied on oily surfaces and does not require either any surface pre-treatment or the application of any adhesion primer. Therefore a minimum joint thickness of about 0.2 mm is required in order to obtain a good adhesion of the adhesive on the substrate.

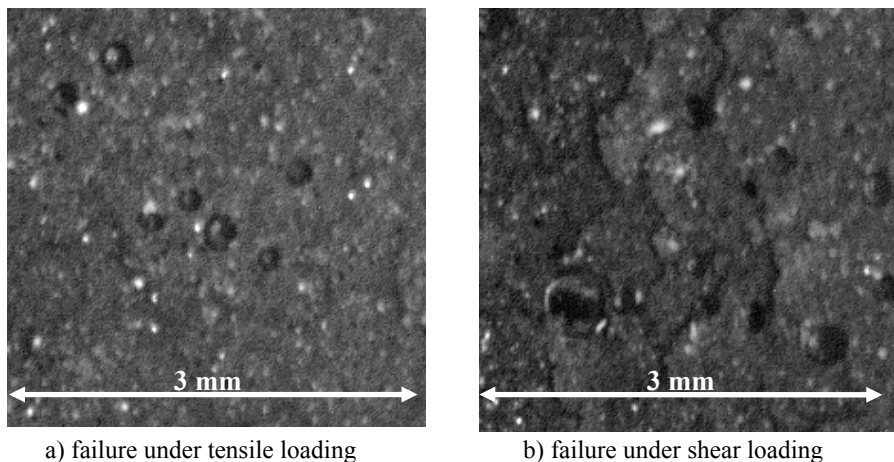


Figure 12. Fracture surface examination under tensile and shear loadings.

Bonded joints were studied using DC04 steel (or aluminium) substrates with a mechanical surface preparation (abrasion with 120 grade abrasive paper and an acetone wipe to remove dust particles followed by careful drying). As the

adhesive is viscous, the cartridge must be pre-heated 20 minutes at 60°C before application on both substrates. The curing conditions are 180°C during 30 minutes followed by a low cooling.

The chemical formulation of this adhesive is based on a stiff epoxy matrix toughened by addition of soft inclusions that confer some additional ductility to the adhesive layer (Figure 12). The adhesive is designed for carrying quasi-static and fatigue loads, but not dynamic or crash loads. For the different quasi-static loadings, cohesive failure is observed for this adhesive. But, the fracture surface examination underlines a different failure mode under tensile and shear loadings (figure 12); the deformation of the inclusions depends on the loading conditions. In automotive applications this adhesive is designed to be combined with spot-welds. However, this chapter focuses on the behaviour of the adhesive alone.

## Tensile Dog-bone Bulk Specimen

A typical specimen used to determine the mechanical behaviour of an adhesive is the EN ISO 527-2 type 5A tensile dog-bone bulk specimen, represented in Figure 13a. The specimen is made following a Sika internal Corporate Quality Procedure (CQP 580-5) (Jousset 2010, [40]). A plate of adhesive is first prepared and pressed between two non-sticking lining papers, taking care not to entrap air. The adhesive thickness is controlled using spacer strips. The adhesive sheet is then cured and placed on a flat surface to be cooled down, afterwards. The shape of the specimen is created by cutting the cured adhesive sheet with a dog-bone shaped punch.

Experimental results are presented in Figure 13b, deformations are obtained from the displacement measurement in the central straight part of the specimen, using a contact extensometer. For the bulk specimens, a displacement rate of the crosshead of the tensile testing machine of 2 mm/min was used. For tensile tests, using thin specimens, a localisation of the deformation is often observed close to defects; thus, quite extensive scatter in the results is found, especially for the failure strain.

Such tests allow the Young's modulus of the adhesive to be determined. Using measurement in two directions the Poisson ratio can also be obtained. It is only possible to estimate the so-called "elastic limit" because of the large influence of defects; but using such tests, it seems difficult to analyse the non linear behaviour. Moreover, as adhesives are often characterised by viscous effects, precise comparisons with results of tests on bonded assemblies require similar strain rates for the adhesive; but the ratio of the bulk specimen length and

the joint thickness in a bonded joint can be larger than 100 (Cognard et al. 2011, [41, 42]). Thus, results for bulk tests are herein only indicative in the comparison with results of bonded joints.

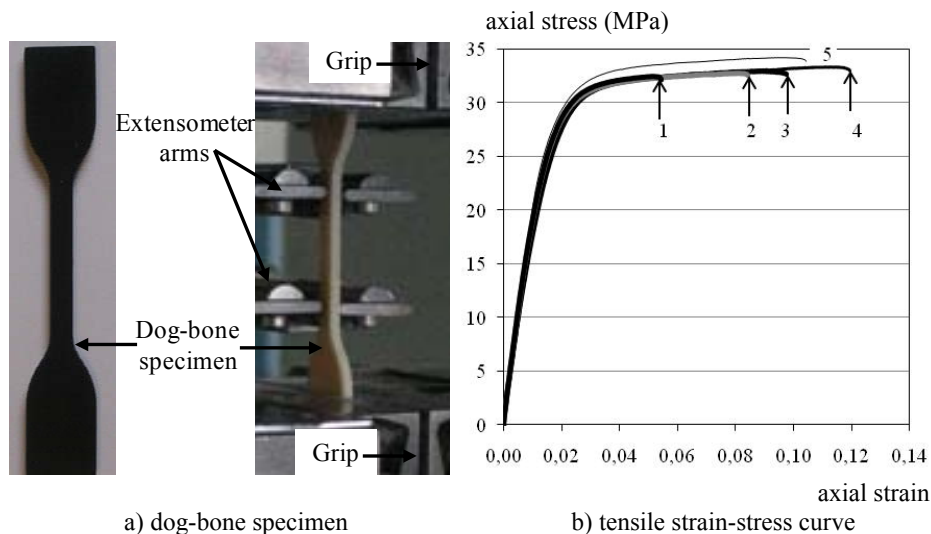


Figure 13. Experimental results of tensile tests with bulk specimens (results for five specimens).

Measuring mechanical properties of an adhesive on bulk specimens or in a joint (in-situ) can give different results (Kinloch 1987, [1]). Indeed, the properties of the confined adhesive can be influenced by the vicinity of substrates during the bonding and curing process (development of an interphase close to substrates) [Montois et al. 2007, [12]; Bouchet et al. 1999, [15]). Defects in bulk specimens can affect the stress-strain response of the specimen (da Silva and Adams 2005, [14]). Thus, the use of bulk specimens does not seem to be adequate to analyse the non-linear mechanical behaviour of an adhesive (Dolev and Ishai 1981, [10]; Jeandreau 1991, [11], Cognard et al. 2011, [41, 42]). Consequently it seems important to experimentally analyze the mechanical properties of an adhesive in a bonded joint under various tensile-shear loads in order to develop accurate material constitutive models.

## EXPERIMENTAL RESULTS UNDER SHEAR LOADS

This section presents comparisons between results from different experimental test setups, some of them designed to greatly limit the edge effects. In order to analyse the different experimental results, numerical analysis of the stress distributions within the adhesive along the bondline under elastic assumption is proposed. In this section, we focus mainly on the adhesive behaviour under monotonic loadings. In order to make the comparison easier, results are presented using the average strain – average shear stress diagram. However, it is important to notice that the stress state is not homogeneous in the adhesive under elastic assumption for the different test setups used. Moreover, the different tests have been done in different laboratories, using different measurement techniques, and using different adhesive batches; thus, a little part of the scatter in the result can be associated to these points.

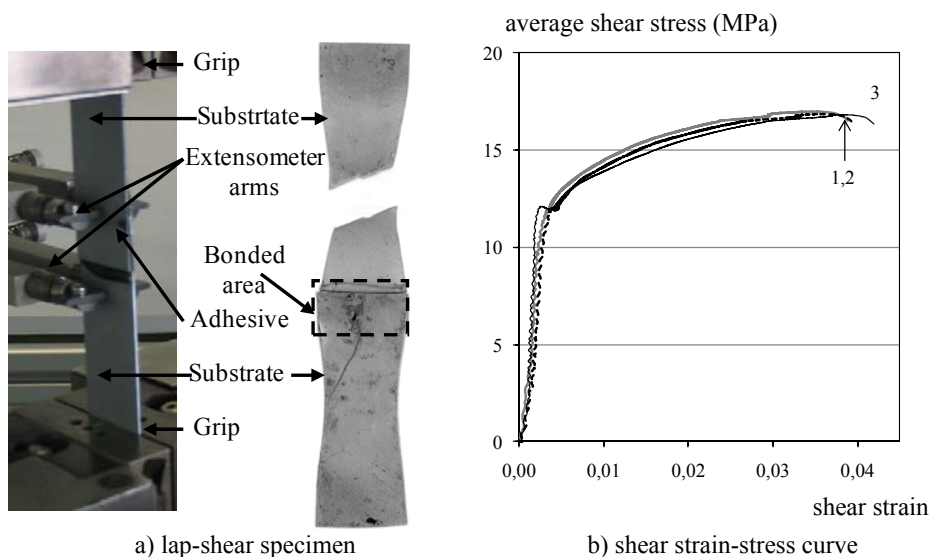


Figure 14. Experimental results of lap-shear specimens (results for three specimens).

### Thin Adherends Lap Shear Test

For the lap-shear tests (NF-EN 1465, ISO4587), substrates with a length of 100 mm and a thickness of 0.8 mm were used. The adhesive thickness was

controlled by inserting glass balls of 0.3 mm diameter over the overlap area of 25.4 mm x 12.5 mm. The displacement rate of the crosshead of the tensile machine was 10 mm/min. The deformation is measured using a contact extensometer (Figure 14). The use of thin substrates leads to a complex behaviour of the test (large deformation of the substrates) which can lead to a complex stress state in the adhesive. Moreover, failure is obtained in the substrates; and at failure the maximum strain in the adhesive is quite low (lower than for the tensile bulk tests, Figure 13). Thus, the numerical analysis of such a test is not easy.

### Thick Adherend Shear Test (TAST)

The thick adherend shear test (TAST) is a straightforward extension of the single lap-shear test which is widely used to evaluate the behaviour of an adhesive under shear (Zgoul and Crocombe 2004, [43]).

Using thick adherends and a short overlap enables the peel stresses, which complicate the single lap-shear test, to be significantly reduced (limitation of the stress concentrations). The test was carried out with the following geometrical parameters: 110 mm specimen length, 20 mm wide substrates, 10 mm thick substrates, 5 mm overlap length and 0.3 mm joint thickness (Figure 15a).

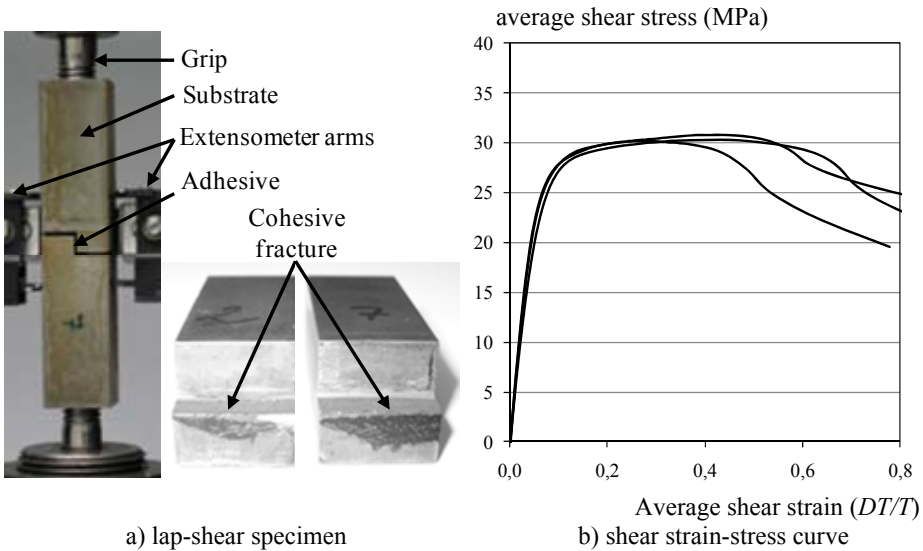
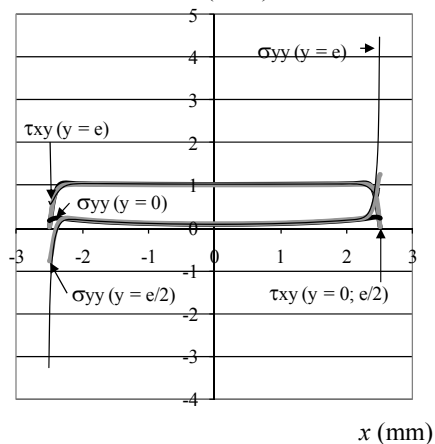


Figure 15. Experimental results of TAST (results for three specimens).

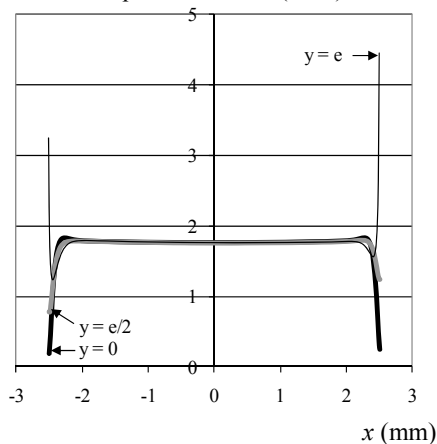
In order to analyze the experimental results, a numerical analysis of the stress distribution under the assumption of linear elastic behaviour was carried out. Figure 16 presents the stress distribution in the adhesive along the  $x$  direction ( $x \in [-2.5 \text{ mm}, 2.5 \text{ mm}]$ ) using different curves associated with the  $y$  position in the joint;  $y = 0$  corresponds to the mid-plane of the joint and  $y = e$  corresponds to a line close to the adhesive-substrate interface ( $T = 2e$  represents the adhesive thickness). The shear stress is mostly constant over the overlap length and throughout the joint thickness. However, quite significant peel stress and von Mises equivalent stress appear close to the joint extremities at the adhesive-substrate interface associated with the influence of edge effects.

Peel and shear stress (MPa)



a) peel and shear stress

von Mises equivalent stress (MPa)



b) von Mises equivalent stress

Figure 16. Numerical results for the Althof test and for an average shear stress of 1 MPa.

Figure 15b presents experimental results for three specimens and one can notice that the differences with the results of the single lap-shear tests with thin substrates; but, the presence of quite high stress concentrations leads to quite large scatter in the results (deformation for the limit point). The relative displacement of the substrates denoted by  $DT$  was measured using a specific extensometer, thus the average adhesive deformation is represented by  $(DT/T)$  where  $T$  is the adhesive thickness.

## Modified TAST

It has been numerically shown and experimentally verified that sharp beaks and cleaned edges of the adhesive can significantly limit the influence of edge effects (Cognard 2008, [28]).

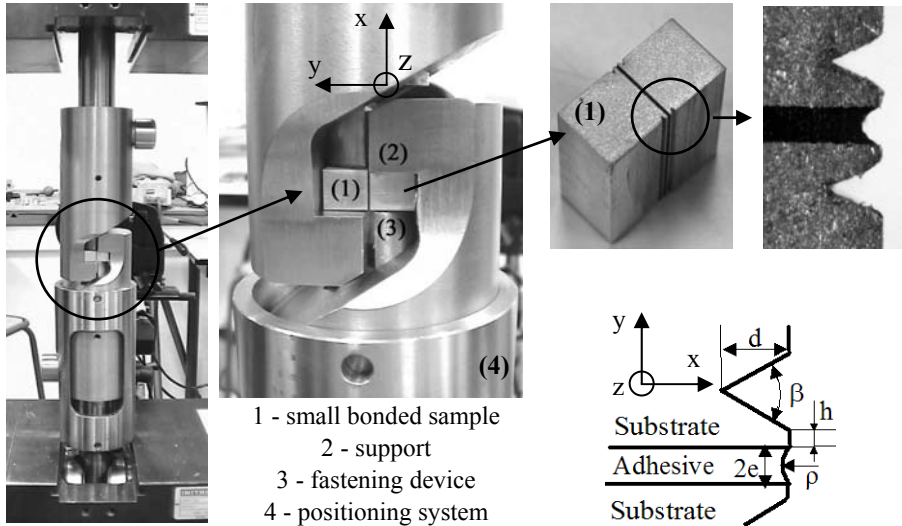


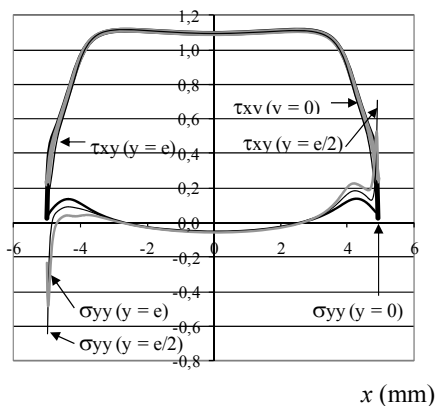
Figure 17. The modified TAST fixture.

Moreover, rigid supports are used to reduce the effect of the support bending observed with single-lap shear specimens. Thus, a modified TAST has been proposed (Figure 17), where the small bonded samples with beaks (1) are mounted in a support (2) and fixed with a fastening device (3). The use of small bonded samples which represent the central part of the TAST (adhesive cross-sectional area:  $S_c = 9.53 \text{ mm} \times 25.4 \text{ mm}$ ) reduces the cost of such tests. A special system (4) is used for a precise positioning of the specimen in the support. The main geometrical parameters and some results can be found in (Cognard and Créac'hacdec 2009, [38]).

Figure 18 represents the stress state in the adhesive, for an average shear stress of 1 MPa, with respect to the  $x$  abscissa ( $x \in [-4.765 \text{ mm}, 4.765 \text{ mm}]$ ). The use of sharp beaks limits to a large extent the stress concentrations associated with edge effects. It can be observed that the level of the peel stress is quite low close to the free edges of the adhesive compared to TAST (Figure 15). Thus, close to the free edges of the adhesive the von Mises equivalent stress is lower than in the middle of the joint (the more stressed part of the adhesive is in the middle of the

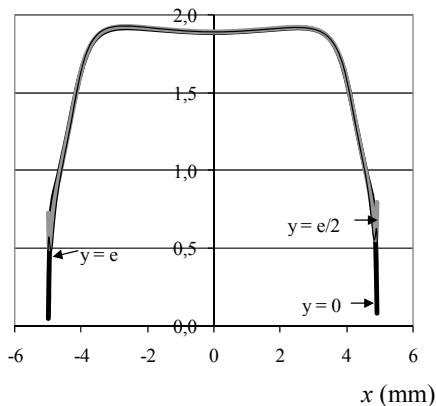
joint) (Cognard and Créac'hadeac 2009, [38]). For this test, a non-contact extensometry system based on image correlation was used to analyze the relative displacement of the substrates  $DT$ ; thus the adhesive deformation is represented by  $(DT/T)$  where  $T$  is the adhesive thickness. Figure 19 represents experimental results. Five specimens were used and it can be seen that the scatter in the results is very low. Compared to the TAST a much larger deformation is observed using the modified TAST which has been designed to considerably limit the influence of edge effects.

Peel and shear stress (MPa)



a) peel and shear stress

von Mises equivalent stress (MPa)



b) von Mises equivalent stress

Figure 18. Numerical results for the Modified TAST with aluminium substrates and for an average shear stress of 1 MPa.

Compared to the TAST (Figure 15b) a much larger deformation is observed using the modified TAST which has been designed to considerably limit the influence of edge effects. The comparison of the experimental results presented in Figures 15 and 19 underlines the influence of stress concentrations on the global response of bonded joints. The maximal average stress and the associated adhesive deformations are larger for the modified TAST than for the TAST. Moreover, it is important to notice that for the modified TAST, under elastic assumption, the average stress underestimates the stress state in the middle of the joint because of the beaks (Figure 18). However, one has also to take into account the influence of possible geometrical defects and parasitic loadings. For the modified TAST, a special system is used (noted (4) in Figure 17) to obtain precise positioning of the specimen in the support. Connections to the tensile testing machine, allowing rotations, are used to prevent parasitic loadings.

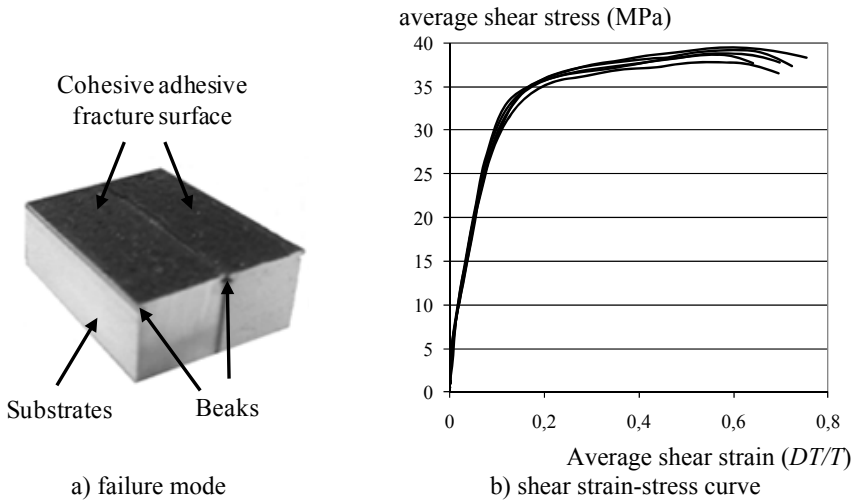


Figure 19. Experimental results for the Modified TAST with aluminium substrates (results for five specimens).

## BEHAVIOUR OF THE ADHESIVE UNDER TENSILE-SHEAR LOADS

Scarf joints (Gacoin et al. 2009, [26]), tensile-torsion tests with tubular substrates (Mahnken and Schlimmer 2005, [7]) or Arcan fixtures (Arcan et al. 1987, [27]; Cognard et al. 2006, [44]) allow the analysis of the tensile-shear behaviour of adhesive, but such specimens are often associated with large stress concentrations.

### The Modified Arcan Device

The design of this modified Arcan fixture (use of beaks, cleaning of the free edges of the adhesive, design of the fastening system...) makes it possible to strongly limit the edge effects and prevents pre-loading of the adhesive (Figure 20) (Cognard et al. 2006, [44]). For this test, a bonded specimen with a rectangular section (10 mm x 65 mm) was proposed. The main parameters defining the geometry of the bonded specimen are such that:  $h = 0.1$  mm,  $d = 0.5$  mm,  $r_0 = 0.8$  mm,  $\rho = 1.5$  e,  $\alpha = 45^\circ$  (Figure 20c).

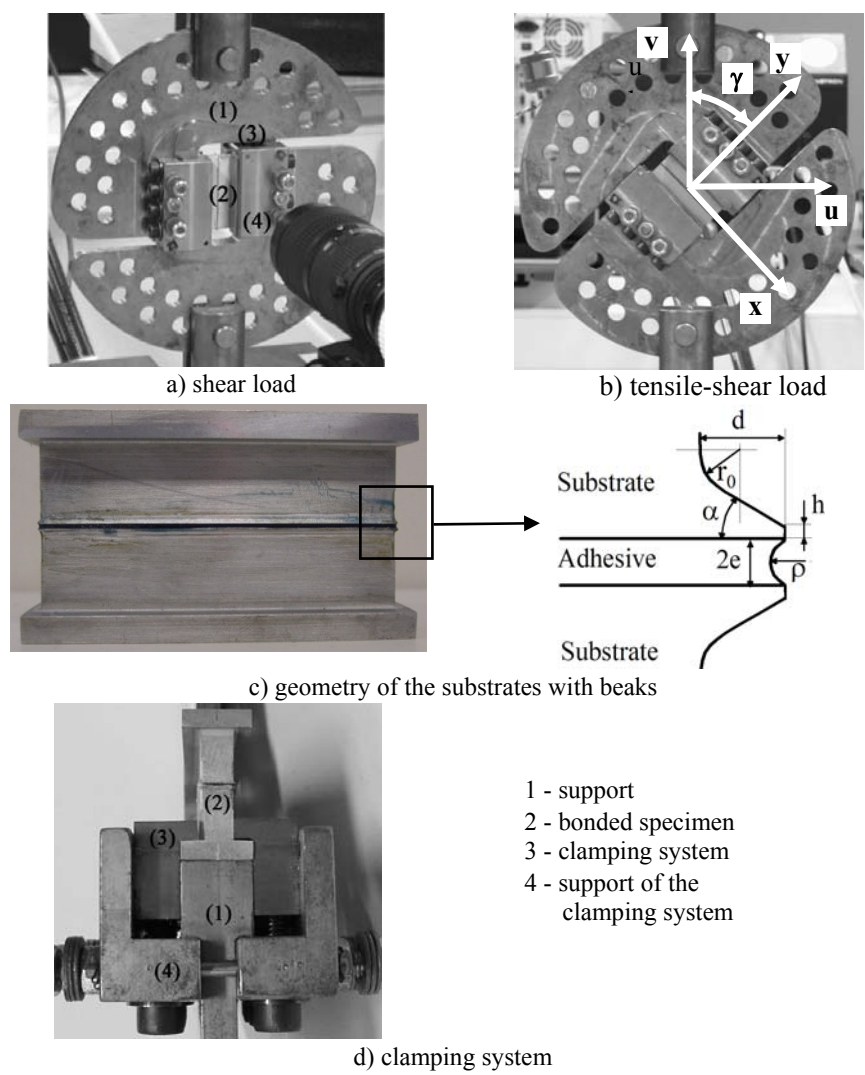
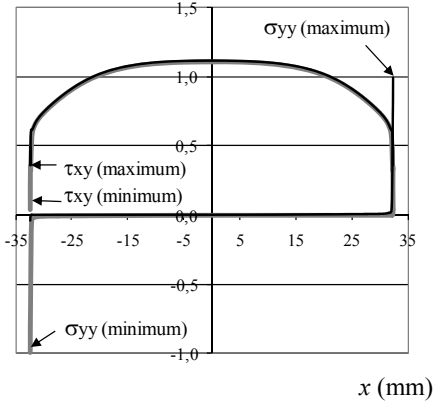


Figure 20. The modified Arcan fixture.

This experimental fixture, associated with a non-contact extensometry system based on image correlation, allowed us to analyze, for radial loadings, the non-linear behaviour of an adhesive joint (Cognard et al. 2006, [44]). Figures 21 and 22 present, for this modified Arcan fixture, the stress distribution in the adhesive, in the case of linear elastic behaviour, under shear and tensile loadings. As for such geometries the maximum stress state can be obtained within the joint

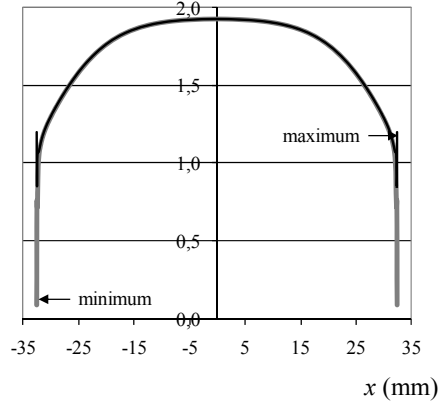
thickness, for a given abscissa  $x$ , only the minimum and maximum values are drawn in order to make analysis of the stress distributions easier.

Peel and shear stress (MPa)



a) peel and shear stress

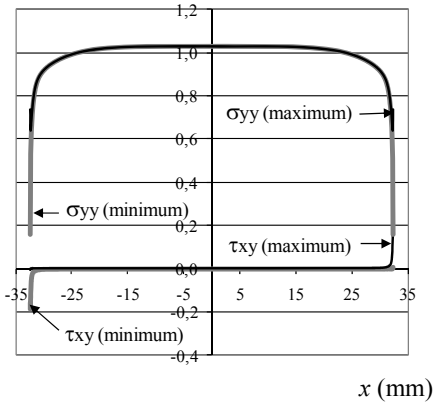
von Mises equivalent stress (MPa)



b) von Mises equivalent stress

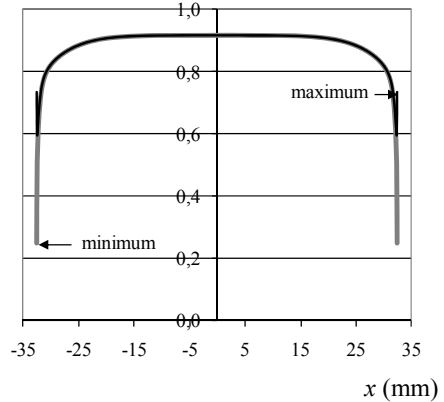
Figure 21. Numerical results for the Modified Arcan under shear loads ( $\gamma = 90^\circ$ ) for a joint thickness of 0.3 mm and for an average shear stress of 1 MPa.

Peel and shear stress (MPa)



Peel and shear stress (MPa)

von Mises equivalent stress (MPa)



von Mises equivalent stress (MPa)

Figure 22. Numerical results for the Modified Arcan under tensile loads ( $\gamma = 0^\circ$ ) for a joint thickness of 0.3 mm and for an average tensile stress of 1 MPa.

For this test, the stress concentrations are larger for steel substrates than for aluminium ones; but, it is important to notice that the von Mises equivalent stress

is maximum in the middle of the overlap length. Moreover, it can be noted that the stress state is not constant in the adhesive, meaning that inverse identification techniques must be used to analyze the experimental results.

## Experimental Results under Tensile-shear Loads

This section highlights some main points of the experimental results obtained under monotonic radial loadings which are useful for developing an accurate numerical model.

We denote by  $DN$  and  $DT$  the relative displacements of both ends of the adhesive joint respectively in the normal and tangential directions in the mean plane of the adhesive joint. The average normal and shear stresses are computed from the components of the applied load in the normal and tangential directions to the mean plane of the adhesive joint.  $FN$  and  $FT$  represent the components of the applied load in the normal and tangential directions. Results are presented in the average stress – average strain diagram in the normal and tangential directions for tensile ( $\gamma = 0^\circ$ ,  $\gamma$  is defined in Figure 19), tensile-shear ( $\gamma = 45^\circ$ ), shear ( $\gamma = 90^\circ$ ) and compression-shear ( $\gamma = 135^\circ$ ) loadings. In order to simplify the presentation, shear stress and shear deformation are represented, in Figure 24, with positive values for compression-shear loadings ( $\gamma = 135^\circ$ ).

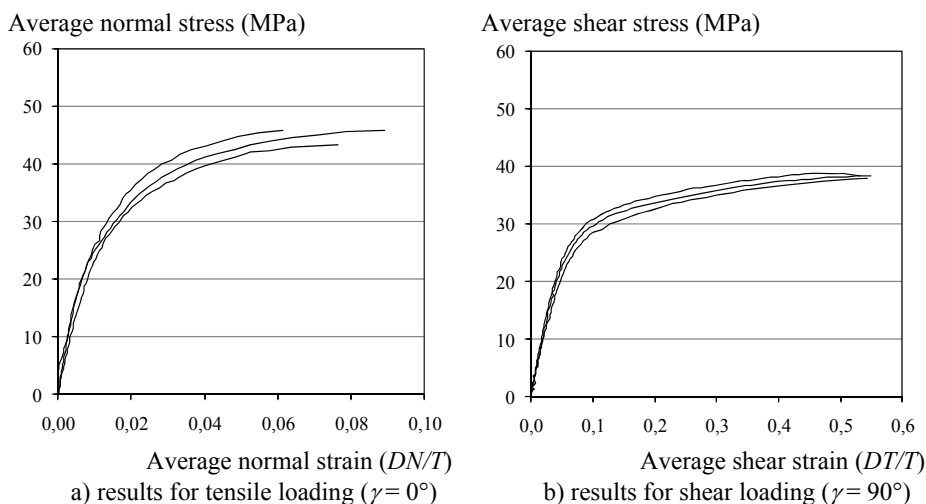


Figure 23. Experimental results for the modified Arcan test under tensile and shear loads.

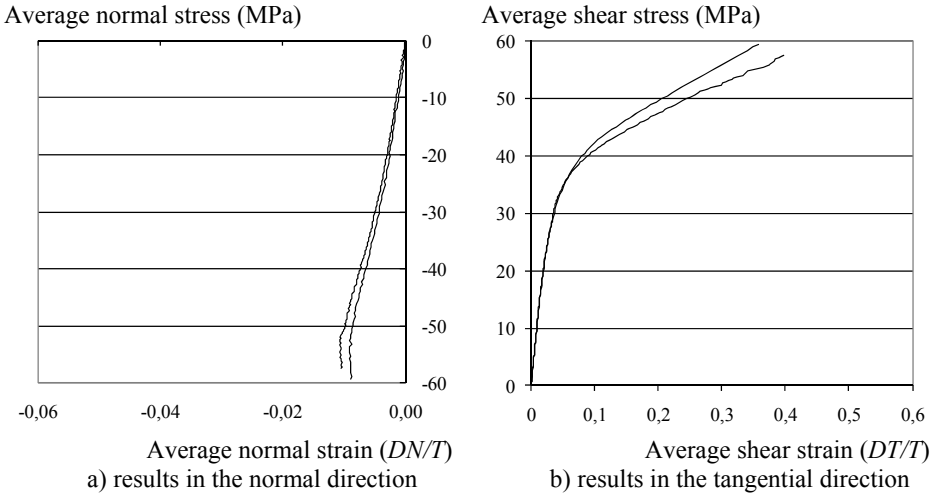


Figure 24. Experimental results for the modified Arcan test under compression-shear.

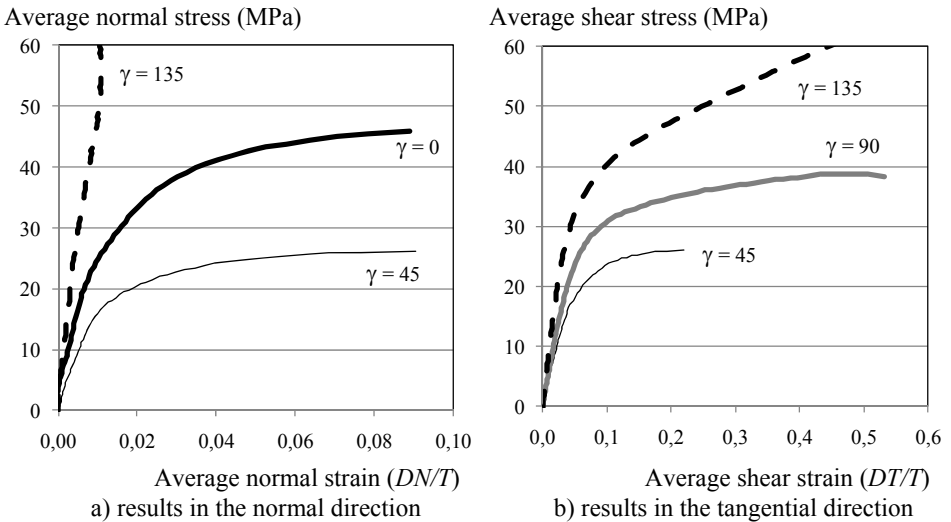


Figure 25. Experimental results for the modified Arcan test for different tensile/compression-shear loads.

Figure 23 represents the scatter in the results for tensile and shear loadings for three tests. It is important to notice that the deformation at failure is much more important in shear direction than in tensile one. The scatter in the results is larger for tensile loads because of the influence of edge effects which are larger for such

loads, especially for steel substrates. Figure 24 presents the results for compression-shear loadings; the presence of inclusions can explain the low deformation under compression. Figure 25 underlines the influence of the tensile/compression-shear loadings on the mechanical behaviour of the joint. These results are useful in order to develop numerical models.

Figure 26 presents the failure modes for different tensile/compression-shear loads with the modified Arcan test; a cohesive failure is obtained for the different loadings.

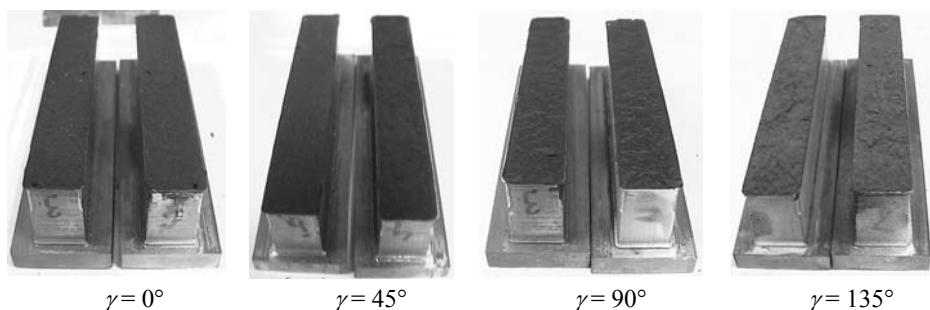


Figure 26. Failure modes for different tensile/compression-shear loads.

## MODELLING OF THE ADHESIVE BEHAVIOUR UNDER MONOTONIC LOADS

The description of the yield surface (elastic limit) for an adhesive, in the case of 3D models, is generally made using the two stress invariants, hydrostatic stress and von Mises equivalent stress (Raghava et al. 1973, [6]; Mahnken and Schlimmer 2005, [7]; Cognard et al. 2010, [45]). Moreover, non-associated flow rules are required to represent the adhesive deformation. It can be noted, in the previous experimental results, that the tangential deformation is much greater than the normal one at failure.

### Equations of the Model

A model formulation has been proposed based on the model of Mahnken and Schlimmer (2005, [7]) and implemented following the method proposed by

Cvitanic et al. (2008, [46]). The main points of the model formulation are recalled in this section (Jousset 2010, [40]; Jousset and Rachik 2010, [47]). The total strain increment  $d\boldsymbol{\varepsilon}$  is additively split into an elastic part  $d\boldsymbol{\varepsilon}^e$  and a plastic part  $d\boldsymbol{\varepsilon}^p$  :

$$d\boldsymbol{\varepsilon} = d\boldsymbol{\varepsilon}^e + d\boldsymbol{\varepsilon}^p \quad (3)$$

The stress increment  $d\boldsymbol{\sigma}$  is related to the elastic strain increment through the elastic constitutive equation:

$$d\boldsymbol{\sigma} = \boldsymbol{D} : d\boldsymbol{\varepsilon}^e \quad (4)$$

where  $\boldsymbol{D}$  is the fourth-order elastic constitutive tensor. The yield function  $F$  is inspired from (Mahnken and Schlimmer 2005, [7]) and has been slightly modified in the form of a square root for numerical integration.

$$F = f - Y \leq 0 \quad \text{with} \quad f = \sqrt{3J_2 + a_1 Y_0 I_1 + a_2 I_1^2} \quad (5)$$

where  $J_2$  is the second invariant of the deviatoric stress,  $I_1$  is the stress first invariant (hydrostatic pressure),  $a_1$  and  $a_2$  are material parameters.  $Y$  is the yield stress that takes into account the strain hardening of the material and  $Y_0$  is its initial value. For the isotropic strain hardening, the evolution of the yield stress with the strain-like state variable  $\bar{\boldsymbol{\varepsilon}}^p$  is described by the following equation:

$$Y = Y_0 + q \left( 1 - e^{-b \bar{\boldsymbol{\varepsilon}}^p} \right) + H \bar{\boldsymbol{\varepsilon}}^p \quad (6)$$

where  $Y_0$ ,  $q$ ,  $H$  and  $b$  are material parameters. The flow rule governing the evolution of the plastic flow is expressed as:

$$d\boldsymbol{\varepsilon}^p = d\lambda \frac{\partial g}{\partial \boldsymbol{\sigma}} \quad (7)$$

where  $d\lambda$  is the plastic multiplier and  $g$  is the flow potential for non associated plasticity. The flow potential has the same form as the yield function:

$$g = \sqrt{3J_2 + a_1^* I_1 Y_0 + a_2^* I_1^2} \quad (8)$$

where  $\bar{a}_1^*$  and  $\bar{a}_2^*$  denote material parameters. As reported in (Mahnken and Schlimmer 2005, [7]) for thermodynamic consistency,  $\bar{a}_1^*$  is taken equal to zero. The strain-like internal variable  $\bar{\varepsilon}^p$  is defined as:

$$d\bar{\varepsilon}^p Y = \sigma : d\varepsilon^p \quad (9)$$

$\bar{\varepsilon}^p$  is associated with the yield function  $f$  defined in equation (5) and is, therefore, different from the equivalent plastic strain associated with the von Mises equivalent stress.

The consistent integration of the constitutive model has been performed based on an implicit backward Euler scheme divided in an elastic predictor and a plastic corrector step. For more details, the reader should refer to (Cvitanic et al. 2008, [46]). The elastic predictor assumes an elastic strain increment resulting in a trial elastic stress tensor  $\sigma^t$ :

$$\sigma^t = \sigma_n + D : \Delta \varepsilon \quad (10)$$

where  $\sigma_n$  denotes the Cauchy stress tensor at the end of the increment  $n$ .  $\Delta \varepsilon$  is the strain increment. The plastic corrector step is activated in the case where the trial state violates the yield condition (Equation 5). Assuming the trial state as the initial condition, a plastic correction step is carried out to find the exact final stress state as well as the correct ratio of elastic and plastic strains in the material. The incremental form of the Equation (5) is described by means of a system of four non-linear algebraic equations:

$$\begin{cases} F(\sigma_{n+1}, Y_{n+1}) & = 0 \\ D^{-1} : (\sigma_{n+1} - \sigma^t) + \Delta \lambda \left( \frac{\partial g(\sigma)}{\partial \sigma} \right)_{n+1} & = 0 \\ Y_{n+1} - \left( Y_0 + q \left( 1 - e^{-b(\bar{\varepsilon}_n^p + \Delta \bar{\varepsilon}^p)} \right) + H(\bar{\varepsilon}_n^p + \Delta \bar{\varepsilon}^p) \right) & = 0 \\ \Delta \bar{\varepsilon}^p f(\sigma_{n+1}) - \Delta \lambda g(\sigma_{n+1}) & = 0 \end{cases} \quad (11)$$

where  $\sigma_{n+1}$  denotes the Cauchy stress tensor at the end of the increment  $n+1$ . The system of Equations (11) can be directly solved using the iterative Newton-Raphson method. This requires solving a system of nine linear equations for each iteration. However, a strategy has been proposed to compute explicitly  $\delta \Delta \bar{\varepsilon}^p$ ,

$\delta\Delta\lambda$ ,  $\Delta\sigma$  and  $\Delta Y$  at each iteration by means of the inversion of a six by six matrix resulting in a shorter computational time (Cvitanic et al. 2008, [46]). This strategy has been adopted here.

The model was implemented in Abaqus under the form of a Fortran UMAT(User MATERIAL subroutine) (Abaqus 2008, [48]).

## Comparison between Experimental Results and Finite Element Analysis

The material constitutive parameters have been identified using an inverse method detailed in (Jousset and Rachik 2010, [47]); results are presented in table 2.

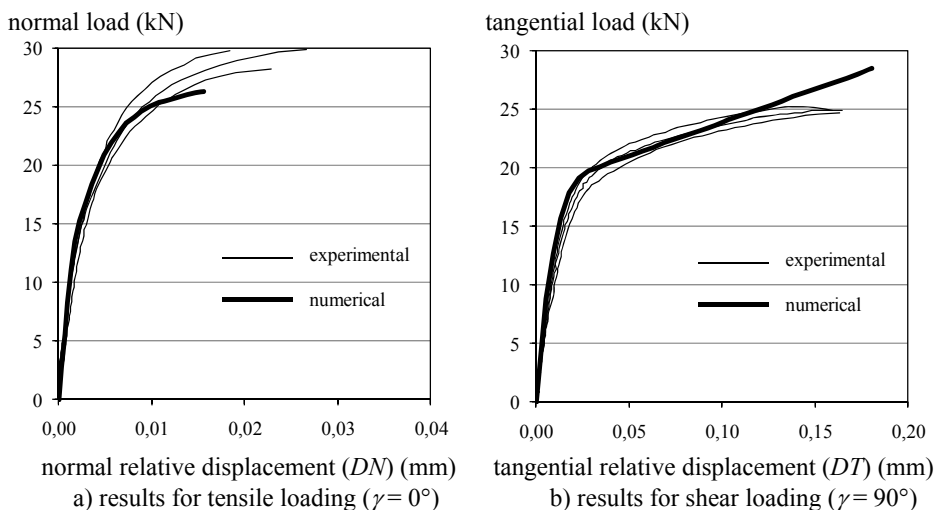


Figure 27. Comparison between experimental and finite element analysis in the load-displacement diagram for modified Arcan tests under tensile loading ( $\gamma = 0^\circ$ ) and shear loading ( $\gamma = 90^\circ$ ).

Figures 27 and 28 show comparison between the experimental and numerical results in the load-displacement diagram. Results are presented for modified Arcan tests under tensile ( $\gamma = 0^\circ$ ), shear ( $\gamma = 90^\circ$ ) and tensile-shear ( $\gamma = 45^\circ$ ) loadings. These results underline the accuracy of the response of the proposed model for proportional monotonic tensile-shear loadings. The modelling of the mechanical response of the adhesive requires the use of pressure-dependent and non-associated numerical models; therefore a large data base of experimental

results under tensile-shear loadings is necessary to identify the material parameters of the model.

Table 2. Material parameters

| $E$<br>(MPa) | $\nu$<br>(-) | $Y_0$<br>(MPa) | $H$<br>(MPa) | $Q$<br>(MPa) | $B$<br>(-) | $a_1$<br>(-) | $a_2$<br>(-) | $a_2^*$<br>(-) |
|--------------|--------------|----------------|--------------|--------------|------------|--------------|--------------|----------------|
| 2120.        | 0.36         | 29.6           | 82.8         | 20.8         | 177.       | 0.186        | 0.300        | 0.128          |

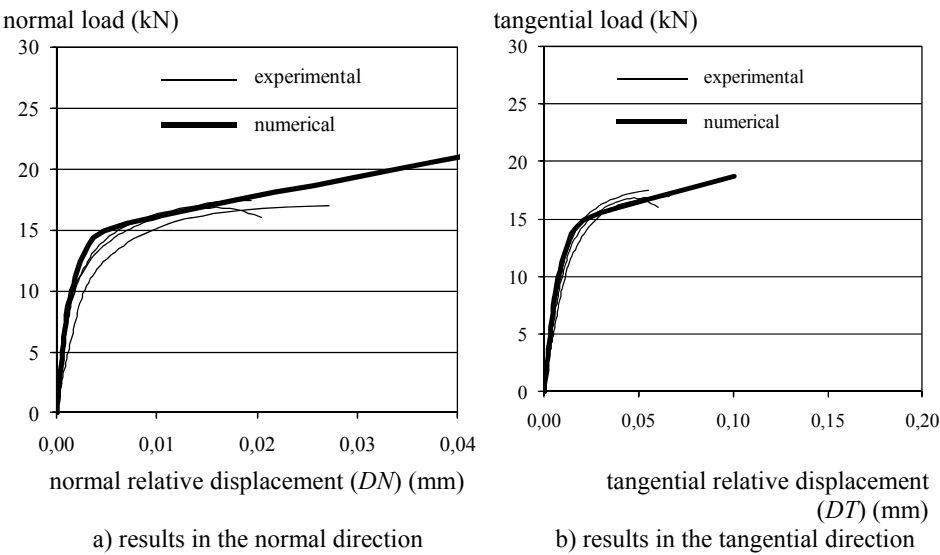


Figure 28. Comparison between experimental and finite element analysis in the load-displacement diagram for modified Arcan tests under tensile-shear loading ( $\gamma = 45^\circ$ ).

The numerical modelling of the modified Arcan tests does not require refined meshes in the joint thickness as the stress concentrations are quite low; herein computations have been done in 3D with solid elements through the joint thickness). Good numerical results are also obtained using interface or cohesive zone models for such applications (Cr  ac  cadec et al 2009, [9]).

## INFLUENCE OF SOME PARAMETERS ON THE BEHAVIOUR OF BONDED JOINTS

This section analyses mainly the influence of the viscous effects of the adhesive starting from experimental results using the modified Arcan setup under various tensile and shear loadings. Moreover, the influence of the adhesive thickness on the mechanical response of the bonded joint is analyzed. These results underline the complex behaviour of bonded joints which have to be taken into account for the design and the optimisation of industrial applications. The experimental results which follow, unless stated otherwise, were realized using steel substrates, an adhesive thickness of 0.3 mm and a displacement rate of the tensile testing machine crosshead of 0.5 mm/min.

### Behaviour under Cyclic Loadings

Figure 29 presents the results of a shear test under monotonic and under cyclic loadings with increasing tensile and shear loads. One can notice a viscoplastic behaviour of the adhesive. Moreover, a reduction of the joint stiffness (associated perhaps with damage) can be noticed for such tensile loadings but not for shear loadings.

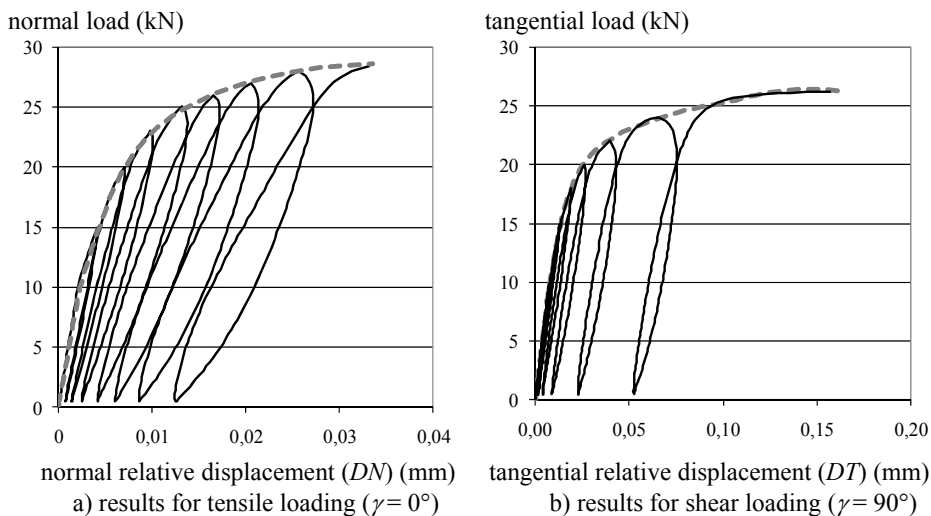


Figure 29. Influence of increasing cyclic loadings under shear loading using the modified Arcan test.

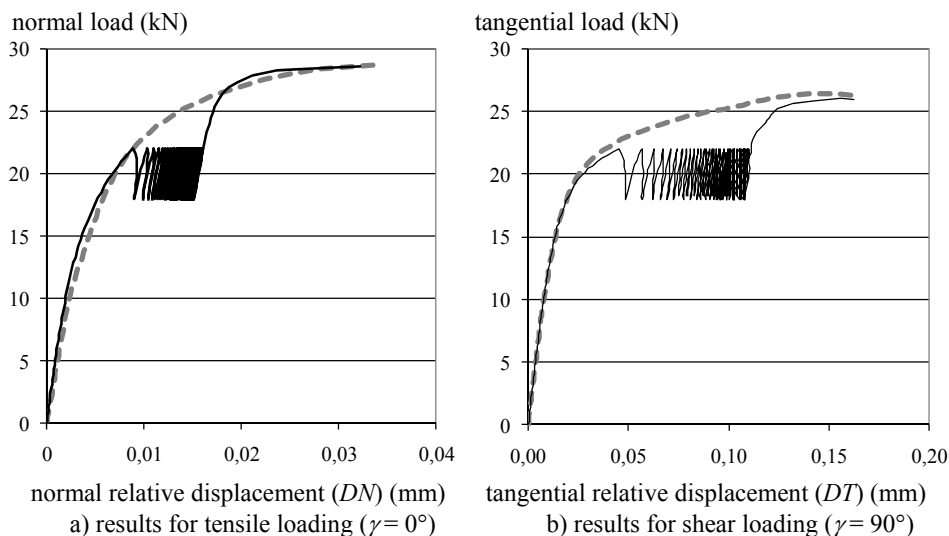


Figure 30. Influence of cyclic loadings under tensile and shear loadings using the modified Arcan test.

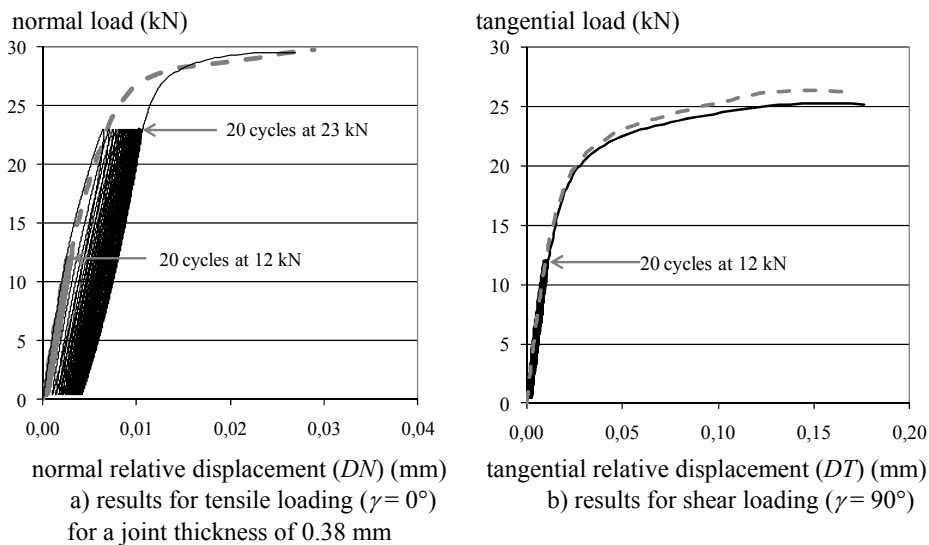


Figure 31. Influence of cyclic loadings under tensile and shear loadings using the modified Arcan test.

For the two loadings, the results are compared with the mechanical response under monotonic loadings, and it can be seen that cyclic responses follow the

monotonic ones for the maximum values (Jousset and Rachik 2010, [47]) (as for different materials). Moreover failure is observed for a given adhesive deformation which depends on the loading type.

Figure 30 presents the behaviour of the bonded joint for tensile and shear tests under monotonic loading and under cyclic loading (40 cycles between 18 and 22kN) followed by a monotonic loading. The low amplitude cyclic loading is applied after a small plastification of the adhesive under monotonic loading. For such cyclic loadings, an increase of the inelastic deformations is observed, which also underlines the influence of viscous effects.

Figure 31 presents results of cyclic loadings under the so called “elastic” limit. These results show that there are small plastic strains for loadings in the so called “elastic” zone behaviour. The inelastic deformation depends on the maximum load of the cyclic loading. Similar results are obtained under tensile-shear loadings (Figure 32).

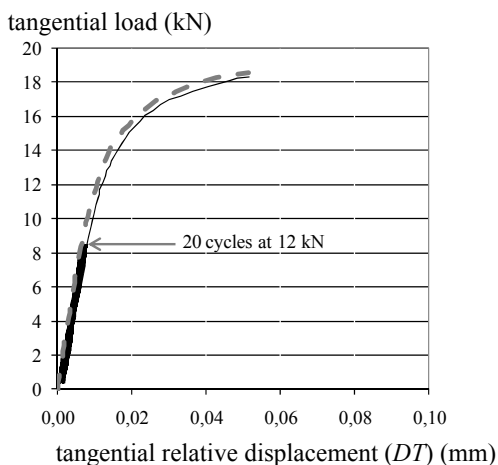


Figure 32. Influence of cyclic loadings under tensile-shear loading ( $\gamma = 45^\circ$ ) using the modified Arcan test (results in the tangential direction).

## Behavior under Complex History Loadings

Figure 33 illustrates the behaviour of the adhesive under complex tensile history loadings including “relaxation” loadings, obtained by blocking the cross-head of the tensile testing machine.

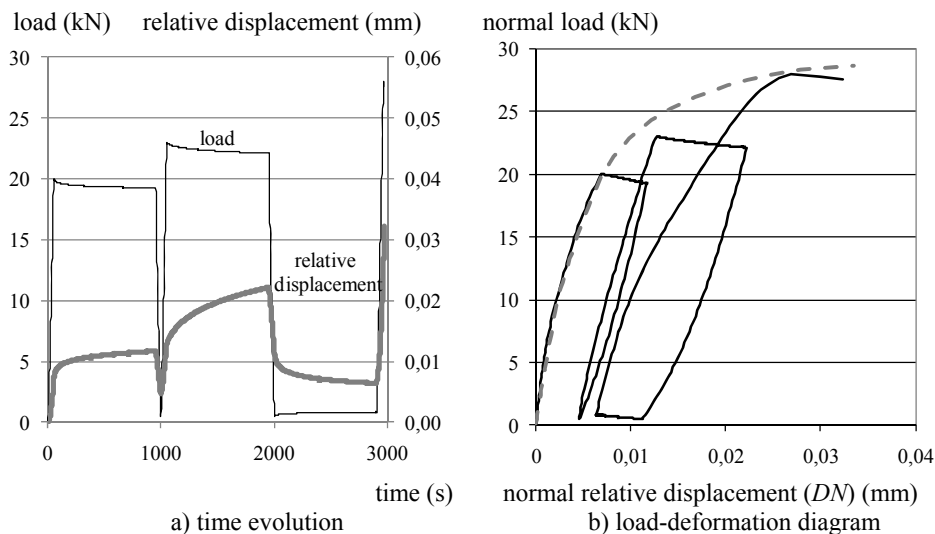


Figure 33. Influence of complex history loadings under tensile loading using the modified Arcan test.

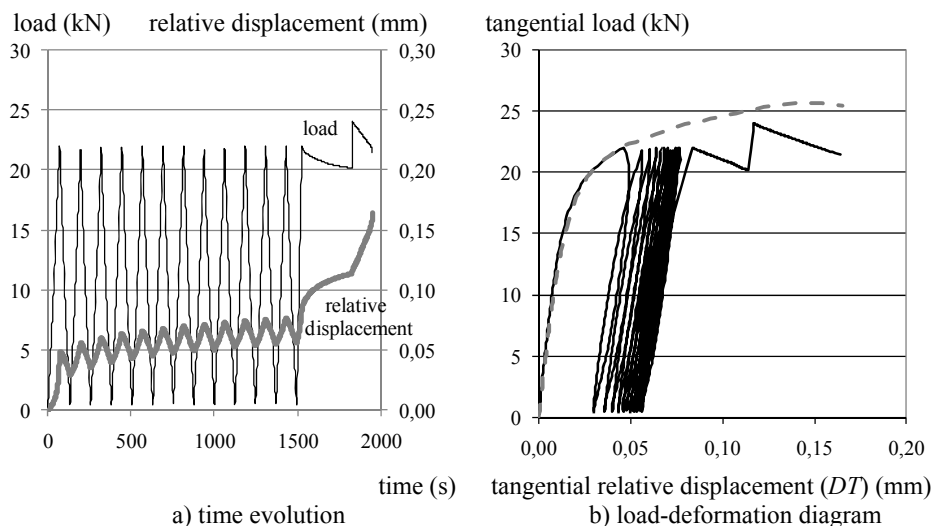


Figure 34. Influence of complex history loadings under shear loading using the modified Arcan test.

Figure 33a presents the time evolution of the load transmitted by the bonded assembly and of the axial deformation of the joint. When blocking the cross-head, we observe an increase of the adhesive deformation and a decrease of the load

transmitted by the joint. Figure 33b represents the mechanical response of this complex history loading in the load-deformation diagram. Figure 34 represents the behaviour of the adhesive under complex shear history loadings including cyclic loadings followed with “relaxation” loadings. Similar results as under tensile loading conditions can be observed.

For the different loadings situations, the maximum envelope of the mechanical response follows the monotonic loading response. Moreover the adhesive deformation at failure depends on the loading type.

### Influence of Joint Thickness for a Given Strain Rate

Experimental load-average strain results are represented in Figure 35 for different joint thickness. A strain rate of 0.028 /s was applied. It appears that an increase of the joint thickness leads to a decrease in both the load and the deformation at failure.

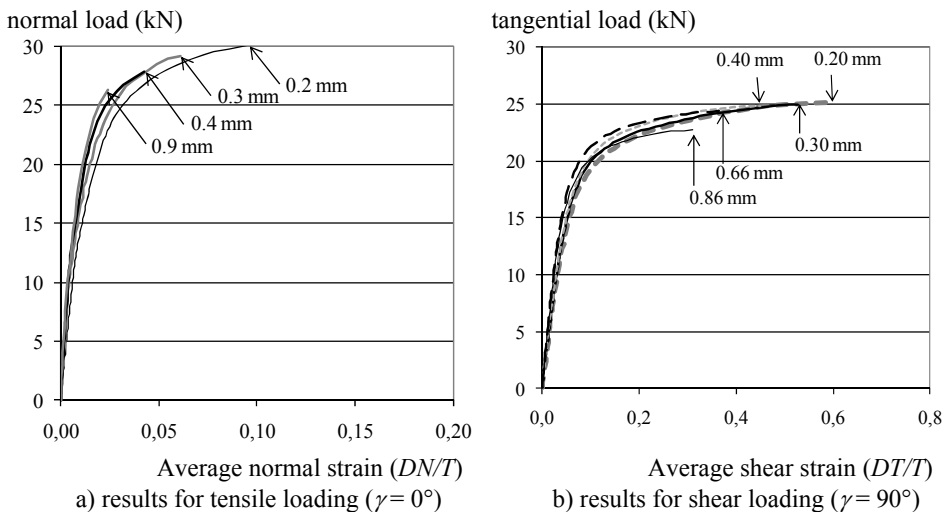


Figure 35. Influence of joint thickness under tensile and shear monotonic loadings using the modified Arcan test for a given strain rate (0.028 /s).

For the modified Arcan setup, an increase of the adhesive thickness is associated with an increase in the stress concentration close to the free edges of the joint which can lead to crack initiation (Davies et al. 2009, [49], Cognard et al.

2010, [37]). This phenomena can be observed for the studied adhesive even with a strong substrate-adhesive interface.

## Influence of the Strain Rate

The influence of the strain rate has been analyzed under tensile and shear loadings (Figure 36). The displacement rate of the tensile testing machine's crosshead was chosen between 0.01 mm/min and 10 mm/min for shear loading and between 0.005 mm/min and 50 mm/min for tensile loading. When submitted to tensile loading, the adhesive deformation can be measured using a classical extensometer, which allows us to use larger displacement rate of the crosshead than those used during measurement based on image correlation techniques. Figure 36 presents experimental results for a large range of strain rate. It can be seen that an increase in the strain rate leads to an increase in the failure load under tensile and shear loadings. However, an increase in the strain rate leads a decrease in the deformation at failure under tensile loading and in an increase of the deformation at failure under shear loadings.

Similar experimental results have been observed for other ductile adhesives (Cognard et al. 2006, [44]; Creac'hcadec and Cognard 2009, [9]; Cognard et al. 2011 [41]).

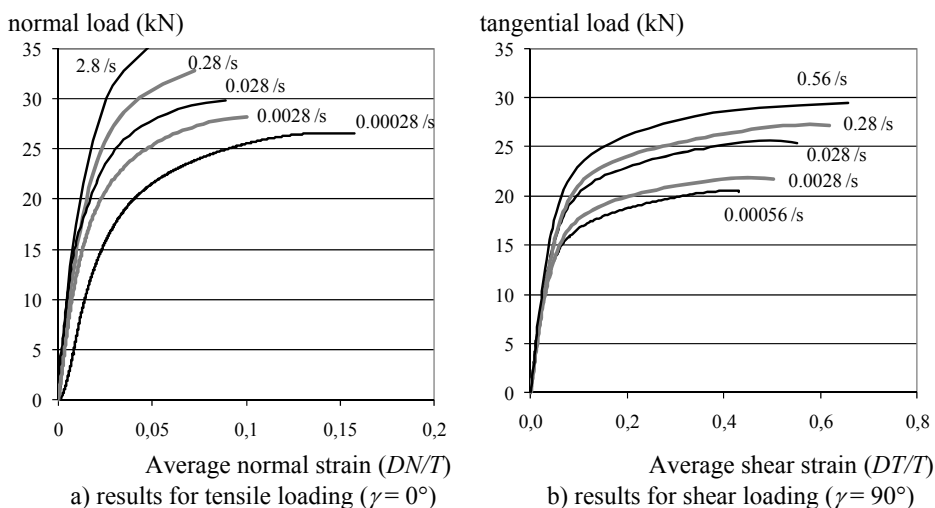


Figure 36. Influence of strain rate under tensile and shear monotonic loadings using the modified Arcan test.

## CONCLUSION

The objective of this study is to define a reliable tool to dimension adhesively bonded assemblies. Experimental and numerical analyses of the mechanical behaviour of bonded joints are made particularly difficult because of stress singularities generated by edge effects. Therefore, to analyse the behaviour of the adhesive in an assembly, experimental fixtures which strongly limit edge effects must be designed in order to obtain reliable data.

The chapter has examined the influence of some parameters on the stress distribution in the adhesive in the case of the usual single-lap shear specimens. Precise finite element computations have been used to analyze the stress state and the stress concentrations in the adhesive under elastic assumption. It has been numerically shown that single-lap joint are characterized with significant stress concentrations at the two ends of the overlap, which are associated with geometrical and material parameters. The stress singularities can contribute to fracture initiation in the adhesive and thus, to an incorrect analysis of the behaviour of the adhesive. Various techniques proposed in the literature only limit the influence of edge effects in the case of single lap-shear setups. Using results of asymptotic analysis, some properties have been presented in order to strongly limit the influence of edge effects. Those properties have been used to develop a modified Arcan setup to accurately analyse the behaviour of an adhesive in an assembly up to failure under a large range of tensile/compression shear proportional loadings.

Three types of experimental tests have been carried out using a structural ductile adhesive which have been designed to obtain a strong substrate-adhesive interface for automotive applications. Tensile tests using bulk specimens are useful to determine the elastic properties (Young's modulus and Poisson's ratio) but possible defects can strongly influence the non-linear behaviour of the bulk specimen. The analyses of experimental results of bonded assemblies presenting large stress concentrations (such as simple lap-shear type specimens) is made particularly difficult because of the complex stress state in the adhesive which can be also very sensitive to defects (geometry, loading ...). Since for such tests, the stress state close to the free edges is quite complex and depends on various geometrical parameters, it is difficult to precisely define the initial elastic limit and the failure limit. However, such tests are interesting to compare the behaviour of different adhesives under complex loadings. The use of experimental devices which considerably limit the influences of edge effects can give more reliable results. Furthermore, they can limit both the scatter in results and the influence of defects.

As the mechanical behaviour of an adhesive in a bonded joint is complex (non-isotropic behaviour) and depends on various parameters (strain rate, temperature, aging ...), a large data base of experimental results under various tensile-compression-shear loadings is necessary to develop models able to accurately predict their behaviour in industrial applications. The utilization of a pressure dependent model using non-associated flow rules has been illustrated for monotonic proportional loadings.

The proposed model must be complemented to describe the various viscous effects observed under cyclic and relaxation loadings to fully represent the experimental results presented in the last part of the chapter. Moreover, since the failure deformation strongly depends on the tensile-shear stress state, reliable tests (i.e. strongly limiting the influence of edge effects) have to be performed under complex non-proportional loadings in order to complete the experimental database. The final aim is to develop accurate numerical models able to optimize the mechanical behavior of complex industrial bonded applications.

## REFERENCES

- [1] Kinloch A.J., *Adhesion and adhesives: science and technology*, Cambridge University Press, 1987.
- [2] Adams R.D. (Ed.), *Adhesive Bonding: Science, Technology and Applications*, Woodhead Publishing Limited, Cambridge, England, 2005.
- [3] da Silva L.F.M. and Öchsner A. (Eds.), *Modeling of Adhesive Bonded Joints*, Springer, Heidelberg, 2008.
- [4] Leguillon D. and Sanchez-Palancia E., *Computation of singular solutions in elliptic problems and elasticity*, Editions Masson, Paris; 1987.
- [5] Wang C.H. and Rose L.R.F., Compact solutions for the corner singularity in bonded lap joints *International Journal for Numerical Methods in Engineering*, 2000, Vol. 20, pp. 145-154.
- [6] Raghava R.S., Cadell R. and Yeh G.S.Y., The macroscopic yield behaviour of polymers, *Journal of Materials Science*, 1973, Vol. 8, pp. 225-232.
- [7] Mahnken R. and Schlimmer M., Simulation of strength difference in elasto-plasticity for adhesive materials, *International Journal for Numerical Methods in Engineering*, 2005, Vol. 63, pp. 1461-1477.
- [8] Rolfes R., Volger M., Ernst G. and Hühne C., Strength of textile composites in multiscale simulation, in *Trends in Computational Structures Technology*, Saxe-Coburg Publications, Stirlingshire, Scotland, 2008, pp. 151-171.

- [9] Créac'hcadec R. and Cognard J.Y., 2D modeling of the behavior of an adhesive in an assembly using a non-associated elasto-visco-plastic model, *Journal of Adhesion*, 2009, Vol. 85, pp. 239-260.
- [10] Dolev G. and Ishai O., Mechanical Characterization of Adhesive Layer in-situ and as Bulk Material, *Journal of Adhesion*, 1981, 12, 283-294 ().
- [11] Jeandreau J.P., Analysis and design data for adhesively bonded joints, *International Journal of Adhesion and Adhesives*, 1991, Vol. 11, pp. 71-79.
- [12] Montois P., Nassiet V., Petit J.A. and Adrian D., Viscosity effect on epoxy-diamine/metal interphases -part II: Mechanical resistance and durability, *International Journal of Adhesion and Adhesives*, 2007, 27 (2), pp. 145-155.
- [13] Lilleheden L., Mechanical properties of adhesives in situ and in bulk, *International Journal of Adhesion and Adhesives*, 1994, Vol. 14, pp. 31-37.
- [14] da Silva L.F.M. and Adams R.D., Measurement of the mechanical properties of structural adhesives in tension and shear over a wide range of temperatures, *Journal of Adhesion Science and Technology*, 2005, 19, pp. 109-141.
- [15] Bouchet J., Roche A.A. and Hamelin P., Internal stresses, Young's modulus and practical adhesion of organic coatings applied onto 5754 aluminium alloy, *Thin Solid Films*, 1999, Vol. 355-356, pp. 270-276.
- [16] Dean G., Crocker L., Read B. and Wright L., Prediction of deformation and failure of rubber-toughened adhesive joints, *International Journal of Adhesion and Adhesives*, 2004, Vol. 24, pp. 295-306.
- [17] Cognard J.Y., Créac'hcadec R., Sohier L. and Davies P., Analysis of the non linear behaviour of adhesives in bonded assemblies. Comparison of TAST and ARCAN tests, *International Journal of Adhesion and Adhesives*, 2008, Vol. 28, pp. 393-404.
- [18] Adams R.D. and Harris J.A., The influence of local geometry on the strength of adhesive joints, *International Journal of Adhesion and Adhesives*, 1987, Vol. 7, pp. 69-80.
- [19] Hildebrand M., Non-linear analysis and optimization of adhesively bonded simple lap joints between fibre-reinforced plastic and metals, *International Journal of Adhesion and Adhesives*, 1987, pp. 261-267.
- [20] Belingardi G., Goglio L. and Tarditi A., Investigating the effect of spew and chamfer size on the stresses in metal/plastics adhesive joints, *International Journal of Adhesion and Adhesives*, 2002, Vol. 22, pp. 273-282.
- [21] Lang T.P. and Mallick P.K., The effect of recessing on the stresses in adhesively bonded single-lap joints, *International Journal of Adhesion and Adhesives*, 1999, Vol. 19, pp. 257-271.

- [22] ASTM D5656-95, American Society for Testing and Materials, West Conshohocken, PA, USA, 1996.
- [23] Althof W., Creep, recovery and relaxation of shear-loaded adhesive bondlines, *Reinforced Plastics & Composites*, 1982, Vol. 1, pp. 29-38.
- [24] Kadioglu F., Vaughn L.F., Guild F.J. and Adams R.D., Use of the thick adherend shear test for shear stress-strain measurements of stiff and flexible adhesives, *Journal of Adhesion*, 2002, Vol. 78, pp. 355-381.
- [25] H. Chai, The effects of bond thickness, rate and temperature on the deformation and fracture of structural adhesives under shear loading, *International Journal of Fracture* 2004, Vol. 130, pp. 497-515.
- [26] Gacoin A., Lestriez P., Assih J., Objois A. and Delmas Y., Comparison between experimental and numerical study of the adhesively bonded scarf joint and double scarf joint: Influence of internal singularity created by geometry of the double scarf joint on the damage evolution, *International Journal of Adhesion and Adhesives*, 2009, Vol. 29, pp. 572-579.
- [27] Arcan L., Arcan M. and Daniel I., SEM fractography of pure and mixed mode interlaminar fracture in graphite/epoxy composites, *ASTM Tech. Publ.*, 1987, 948, pp. 41-67.
- [28] Cognard, J.Y., Numerical analysis of edge effects in adhesively-bonded assemblies. Application to the determination of the adhesive behaviour, *Computer & Structures*, 2008, Vol. 86, pp. 1704-1717.
- [29] Cognard J.Y., Devaux H. and Sohier L., "Numerical analysis and optimisation of cylindrical adhesive joints under tensile loads", *International Journal of Adhesion and Adhesives*, 2010, 30, pp. 706-719.
- [30] CAST3M documentation, [www.cast3m.cea.fr/cast3m](http://www.cast3m.cea.fr/cast3m).
- [31] Cheikh M., Coorevits P. and Loredó A., Modelling the stress vector continuity at the interface of bonded joints, *International Journal of Adhesion and Adhesives*, 2001, Vol. 22, pp. 249-257.
- [32] Goncalves J.P.M., Moura M.F.S.F. and de Castro P.M.S.T., A three-dimensional finite element model for stress analysis of adhesive joints, *International Journal of Adhesion and Adhesives*, 2002, Vol. 22, pp. 357-365.
- [33] da Silva L.F.M., das Neves P.J.C., Adams R.D. and Spelt J.K., Analytical models of adhesively bonded joints – Part I: Literature survey, *International Journal of Adhesion and Adhesives*, 2009, Vol. 29, pp. 319-330.
- [34] Yan Z.M., You M., Yi X.S., Zheng X.L. and Li Z., A numerical study of parallel slot in adherend on the stress distribution in adhesively bonded aluminium single lap joint, *International Journal of Adhesion and Adhesives*, 2007, Vol. 27, pp. 687-695.

- [35] Reedy E.D. and Guess T.R., Comparison of butt tensile strength data with interface corner stress intensity factor prediction, *International Journal of Solids Structures*, 1993, Vol. 30, pp. 2929-2936.
- [36] Leguillon D., Laurencin J. and Dupeux M., Failure initiation in an epoxy joint between two steel plates, *European Journal of Mechanics A/Solids*, 2003, Vol. 22, pp. 509-524.
- [37] Cognard J.Y., Créac'hcadec R., Sohier L. and Leguillon D., Influence of adhesive thickness on the behaviour of bonded assemblies under shear loadings using a modified TAST fixture, *International Journal of Adhesion and Adhesives*, 2010, Vol. 30, pp. 257-266.
- [38] Cognard J.Y. and Créac'hcadec R., Analysis of the non linear behaviour of an adhesive in bonded assemblies under shear loadings. Proposal of an improved TAST, *Journal of Adhesion Science and Technology*, 2009, Vol. 23, pp. 1333-1355.
- [39] Sika, SikaPower 490/7 structural metal adhesive for spot weld bonding, Product data sheet 2009.
- [40] Jousset P., Constitutive modelling of structural adhesives, experimental and numerical aspects, Ph.D. Dissertation 2010, Université de Technologie, Compiègne, France.
- [41] Cognard J.Y., Créac'hcadec R., da Silva L.F.M., Teixeira F.G., Davies P. and Peleau M., Experimental analysis of the influence of hydrostatic stress on the behaviour of an adhesive using a pressure vessel, *Journal of Adhesion*, 2011 (under press).
- [42] Cognard J.Y., Bourgeois M., Créac'hcadec R. and Sohier L., Comparative study of the results of various experimental tests used for the analysis of the mechanical behaviour of an adhesive in a bonded joint, *Journal of Adhesion Science and Technology*, 2011 (under press).
- [43] Zgoul M. and Crocombe A.D., Numerical modelling of lap joints bonded with a rate-dependent adhesive, *International Journal of Adhesion and Adhesives*, 2004, Vol. 24, pp. 355-366.
- [44] Cognard J.Y., Davies P., Sohier L. and Créac'hcadec R., A study of the non-linear behavior of adhesively-bonded composite assemblies, *Composite Structures*, 2006, Vol. 76, pp. 34-46.
- [45] Cognard J.Y., Créac'hcadec R., Maurice J., Davies P., Peleau M. and da Silva L.F.M., Analysis of the influence of hydrostatic stress on the behaviour of an adhesive in an assembly, *Journal of Adhesion Science and Technology*, 2010, Vol. 24, pp. 1977-1994.

- [46] Cvitanic V., Vlak F. and Zeljan L., A finite element formulation based on nonassociated plasticity for sheet metal forming, *International Journal of Plasticity*, 2008, Vol. 24, pp. 646-687.
- [47] Jousset P. and Rachik M., Pressure-dependent plasticity for structural adhesive constitutive modeling, *Journal of Adhesion Science and Technology*, 2010, Vol. 24, pp. 1995-2010.
- [48] Abaqus reference manuals version 6.8. Simulia, Providence, RI, USA, 2008.
- [49] Davies P., Sohier L., Cognard J.Y., Bourmaud A., Choqueuse D., Rinnert E. and Créac'hcadec R., Influence of bond line thickness on joint strength, *International Journal of Adhesion and Adhesives*, 2009, Vol. 29, pp. 724-736.



## *Chapter 2*

# **PRESSURE-SENSITIVE ADHESIVES**

*Zbigniew Czech and Agnieszka Kowalczyk*

West Pomeranian University of Technology, Szczecin, Poland

## **1. PRESSURE-SENSITIVE ADHESIVES (PSA)**

Since their introduction half a century ago, pressure-sensitive acrylic adhesives (PSAs) have been successfully applied in many industrial fields. They are used in self-adhesive tapes, labels and protective films as well as in dermal dosage systems for pharmaceutical applications, in biomedical electrodes, the assembly of automotive parts, toys, and electronic circuits and keyboards. In the last fifty years or so, pressure-sensitive adhesive have made tremendous strides from what was virtually a black art to what is now a sophisticated science. So much so that both the few larger manufacturers of pressure-sensitive adhesive articles and their even larger suppliers now use very expensive equipment to study pressure-sensitive adhesive behavior: tack, adhesion and cohesion.

### **1.1 Definition**

Pressure-sensitive adhesives (PSA) are nonmetallic materials used to bond other materials, mainly on their surfaces through adhesion and cohesion [1]. The difference between pressure-sensitive adhesives and other adhesives, such as contact adhesives, is in the permanent surface stickiness of the pressure-sensitive adhesives before, or after, the application. Pressure-sensitive adhesives (PSA)

have been defined as being adhesives, which in the dry state are aggressively and permanently tacky at room temperature and firmly adhere to a variety of different surfaces upon contact without the need of more than finger or hand pressure. Adhesion and cohesion are phenomena, which may be described thermodynamically and chemically, but actually they cannot be measured precisely. It was shown [2] that the most important bonding processes are bonding by adhesion and bonding with pressure-sensitive adhesives.

## 1.2 Polymer Groups for Manufacturing of Pressure-Sensitive Adhesives

The versatility of polymer chemistry is inherently useful in the design of high performance pressure-sensitive adhesives. A broad raw material base and a versatility of polymerization processes lend themselves to design of base polymers with unique properties.

Two important features contribute to the usefulness of a polymer in adhesive applications. The glass transition temperature ( $T_g$ ) of the polymer should ideally fall in the range between  $-70^\circ\text{C}$  and  $-25^\circ\text{C}$ , and the structure of the polymer should be completely amorphous [3]. The glass transition temperature is the main issue for adhesion properties of various polymers, allowing the selection of raw materials for PSAs applications. It is specific for polymers, but also reveals important information about the suitability of the homopolymers as pressure-sensitive adhesive, which is synthesized from various components. Its value defines the tack of PSAs; a low  $T_g$  is a prerequisite for tacky materials. On the other hand the  $T_g$  alone does not permit to obtain a real image of the adhesive performance [4].

Various types of polymers are commercially available for manufacturing of pressure-sensitive adhesives and self-adhesive articles. The most popular PSA systems are acrylics, natural and synthetic rubbers, silicones, polyurethanes, polyesters, polyether and EVA (ethylene-vinyl acetate) copolymers (Figure 1)

### 1.2.1 Solvent-borne Pressure-Sensitive Adhesives

Pressure-sensitive adhesives can be synthesized and applied in forms as a solvent-borne, as a water-borne (dispersions) and as a solvent-free system.

The markets and technology of high performance solvent-borne pressure-sensitive adhesives are still expanding. The growing market is the result of expansion in both current and new application areas. The increased trend to utilize PSA technology, coupled with versatile polymer chemistry, has created a

dynamic, expanding and challenging market. The versatility of polymer chemistry is inherently useful in the design of high performance PSAs. A broad raw material base and a versatility of polymerization processes lend themselves to design of base polymers with unique properties. The design parameters utilized to produce high performance solvent-borne adhesives include monomer selection, selection of solvents, initiators, high molecular weight, new polymerization methods, new modification methods, new crosslinking agents and new crosslinking kind and technology [6].

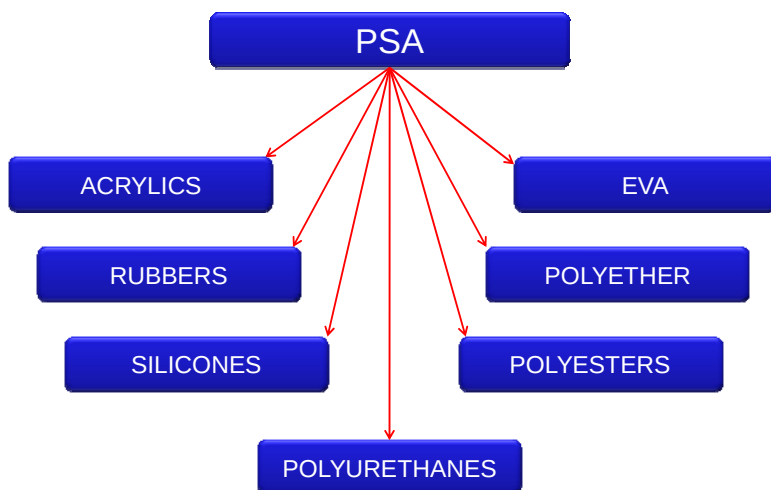


Figure 1. Polymer classes as potential raw materials for the manufacture of PSA.

The media applied for radical polymerization of monomers suitable for PSA synthesis are single organic solvents or their mixtures whose molecules buffer the heavily exothermic polymerization reaction. The selection of suitable solvents is distinctly limited due to following requirements. The solvent has to be: inexpensive, reclaimable, absolutely inert and has to have the proper boiling point between 50°C and 120°C, a relatively low transfer constant and a good solvency for synthesized polymers.

The last mentioned points on the check list for solvents influence the molecular weight being crucial for the entire properties of pressure-sensitive adhesives which should be as high as possible. The higher the boiling point of the solvent the more the properties decrease. Per se very low molecular weights bring about solvents with a high transfer constant, such as petrol with special boiling point. This deficiency can be compensated to a great extent by a versed

conduction of the polymerization process. Such endeavors make sense since aliphatic mixtures particularly meet the first three items of the above catalogue of requirements best [7].

In pressure-sensitive acrylic adhesive solvents available on the market, only a small group of solvents may be found which is not surprising: ethyl acetate, special boiling point petrol (between 60 and 95°C), n-hexane, toluene and acetone.

Specific design parameters are used to achieve desired surface properties of tack and peel in combination with the bulk property of cohesive strength. The balance of these properties is needed for high performance products [8].

### ***1.2.2. Water-borne Pressure-Sensitive Adhesives***

Dispersion of self-adhesive polymers in aqueous media involves the same factors as in organic solvents such as wetting and stabilization. However, the unique properties of water add extra complications. First, the surface of water is high, so there is more likely to be a problem in wetting the surface of low-polarity polymer particles. Second, in some cases, water interacts strongly with the surface of polymers; therefore, the anchor groups on the stabilizers have to interact more strongly with the pigment surface to compete with water. Innovations in adhesive emulsion technology are continuing to impact the development of new water-borne pressure-sensitive adhesives. In particular, products can now be designed that have unique adhesion/cohesion balance, higher heat resistance, and improved humidity resistance. Such advances permit polymer dispersions to be used in very demanding applications where only more expensive, less environmentally friendly solvent-polymer technology has met the requirements. Even in cases where performance of water-borne technology is well established, additional process innovations have led to the development of PSAs that can be coated at higher speeds with faster drying rates thereby reducing cost-in-use [9]. Product innovation pertains to one of the time-tested challenges for water-borne PSA systems to much the cohesive strength and resistance properties of solvent PSA systems while still providing the environmental impact and handling advantages that come with water-borne adhesives. Over the years, various techniques have been explored to tackle the adhesion-cohesion balance of water-borne PSAs. One approach has been to crosslink a soft polymer backbone characterized by low  $T_g$ . The resultant systems provide adequate cohesion but often at the expense of tack and peel. Tackification of a high-cohesive polymer has been another commonly used approach. In the case of water-borne PSA systems it is very important to understand the basic film formation mechanism and the relationship between particle morphology and visco-elastic properties. The goal of water-born adhesive

technology is the manufacturing of aqueous PSAs which are comparable to solvent-borne systems [10].

Drying water-borne systems can be very fast, particularly when the web allows high temperature (e.g. release paper or release film). Explosion hazards do not exist. However, wetting of the web is often a tricky problem and much work is carried out in the area of wetting agents to improve this and minimize effects on performance. Most acrylic PSAs are fairly hard and cause no problems in slitting or diecutting, unless they are highly tackified [11].

### ***1.2.3 Solvent-free Pressure-Sensitive Adhesives***

Solvent-free PSAs are known on the market in form of hot-melts, warm-melts, room temperature coatable low viscosity systems (LVS) and photoreactive UV-crosslinkable prepolymers.

Hot-melt PSAs have become very popular and have gained importance in all areas of adhesive usage in the last decade because of their superior application properties and due to environmental concerns about solvent-borne adhesives. These are 100% solid thermoplastic compounds that contain neither solvent nor an aqueous carrier for the active adhesive components. The traditional solvent-free PSAs deficiencies of hotmelt PSAs are due to the use of relatively low molecular weight polymers, which result in uncrosslinked state in limited heat and plasticizer resistance. Hot-melt PSAs are carrier-free systems where formulating is necessary in order to improve the adhesive, coating and end-use properties, mostly by changing the visco-elastic properties of the pure and bulky components [12].

Warm-melt crosslinkable acrylic PSAs are liquids with coatable viscosity at temperatures between 60 and 90°C. The development and the various opportunities of solvent-free UV-crosslinkable warm-melt PSAs showed the possibility of manufacturing of these systems. The polymer chains of this polymer warm-melt PSAs are carefully controlled in molecular weight and distribution to flow at a relatively sharp and low temperature. Their viscosities drop rapidly on heating to enable processing at elevated temperature. Polymers, which are at the upper viscosity limit when processed as a hot-melt, does not have a sufficiently high molecular weight for satisfactory PSAs performance. The based polymer must either have a very high molecular weight or be crosslinked by additional chemical bonds to exhibit good adhesive and cohesive properties

The photoreactive UV-crosslinkable solvent-free polymeric low viscosity systems (LVS) are at room temperature coatable liquids adhesive with viscosity in the range of 1 to 15 Pa.s. UV-crosslinkable at room temperature coatable polymeric PSAs are a relatively new concept of solvent-free adhesive systems.

The photoreactive solvent-free polymeric low viscosity systems (LVS) allow for coating at ambient temperatures, de facto at room temperature, using conventional roll coating equipment. The compositional aspects of UV-crosslinkable polymeric LVS technology are proprietary, but all are solutions of a high molecular weight of basic polymer containing UV-reactive diluents. After UV irradiation, in the presence of external photoinitiator the photoreactive diluents react to form a polymer structure that becomes an integral part of the polymer PSA. The commonly used reactive diluents are acrylated urethanes, acrylated polyesters, typical acrylate monomers such as n-butyl acrylate, 2-ethylhexyl acrylate, ethoxylaed acrylates, multifunctional acrylates, unsaturated polyether and other photoreactive elastomeric oligomers (Figure 2).

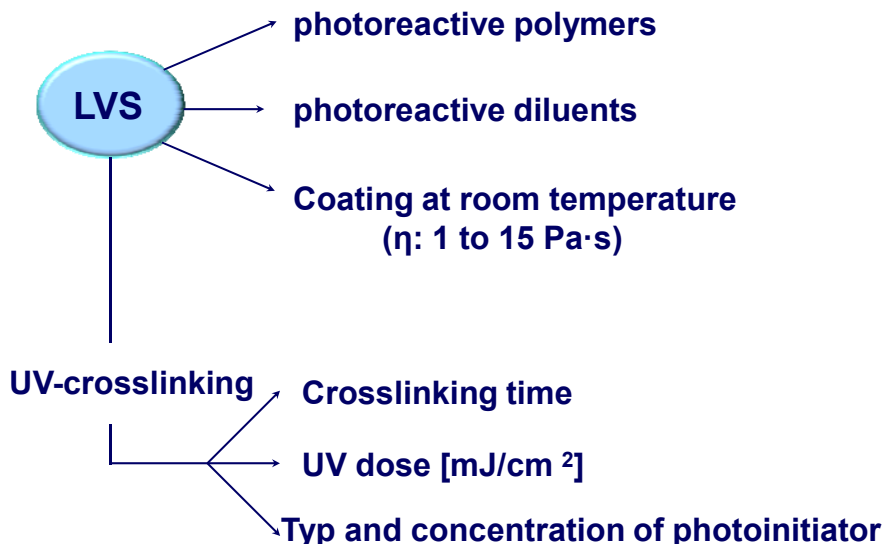


Figure 2. Photoreactive solvent-free polymeric low viscosity systems.

The properties of UV crosslinkable polymeric LVS in form of self-adhesive articles are of course dependent on composition kind, UV dose and UV-crosslinking time.

### 1.3 Properties of Pressure-Sensitive Adhesives

The term pressure-sensitive describes adhesives, which in the dry form are aggressively and permanently tacky at room temperature and firmly adhere to a

variety of dissimilar surfaces upon mere contact, without the need of more than finger or hand pressure. Polymers employed as PSAs have to fulfil partially contradictory requirements; they need to adhere to substrates, to display high shear strength and peel adhesion, and not leave any residue on the substrate upon debonding. In order to meet all these requirements, a compromise is needed. When using PSAs there appears another difference with wet adhesives, namely the adhesive does not change its physical state because film forming is inherent to PSAs. Thus PSAs used in self-adhesive materials are adhesives which through their visco-elastic fluid state, can build up the joint without the need to change this flow state during or after application. On the other hand, their fluid state allows controlled debonding giving a temporary character to the bond. Because of the fluid character of the bonded adhesive, the amount of adhesive (i.e., the dimensions of the adhesive layer) is limited; the joint works as a thin-layer tape, laminate or composite. The solid state components of the tape exert a strong influence on the properties of the adhesive in the composite. Therefore, there exists a difference between the measured properties of the pristine adhesive, and of the adhesive enclosed within the laminate.

The properties, which are essential in characterizing the nature of PSAs comprise: tack, peel adhesion, and shear. The first measures the adhesive's ability to adhere quickly, the second its ability to resist removal through peeling, and the third its ability to hold in position when shear forces are applied [13].

### ***1.3.1 Tack***

Tack, other known as initial adhesion, is defined as “the property of a material which enables it to form a physical bond of measurable strength immediately upon contact with another surface”. Tack is often considered and known in everyday language as stickiness, which means how well a finger sticks to the pressure-sensitive adhesive layer following only slight pressure and short dwell time and withdraw from the adhesive. Tack has been one of the favorite subjects of theorists over many years, often resulting in the derivation of complex formulae in an attempt to explain the property. Nevertheless, tack is still considered and rated by many as how well a pressure-sensitive adhesive sticks to the finger following only slight pressure and short dwell time. While in many cases this can be an approximate measure, this method is badly flawed in that it is highly subjective [14].

When a pressure-sensitive adhesive is applied to a surface, it takes time for that adhesive to wet out the surface until optimum contact area and adhesion is achieved. This time may be a small fraction of second, or may take days or even weeks. The wetting process can be aided by the degree of pressure applied and the

length of time given to that pressure. The rate at which wetting takes place varies inversely with the amount of surface still available for wetting. Because the rate of wettability can be considerably accelerated by applied pressure, in a number of tests this application pressure is reduced to a minimum to increase the sensitivity of the test.

Tack tests are many and varied. However if they are all carefully examined they will be seen to be unique adhesion tests, each with its own method of application to a test surface, applied pressure, unique geometry, and rate of removal. A point in time is chosen during the wettability phenomenon when the adhesive is stripped from the test surface: the force required to do so is considered a measure of tack. Were the test to be repeated, but to allow optimum wetting, a comparison of the two results would be a better indication of how quickly the adhesive was capable of wetting out the surface. Note that an adhesive system can wet out the surface quite quickly, but if the final adhesion is low, then a low tack value will still be apparent.

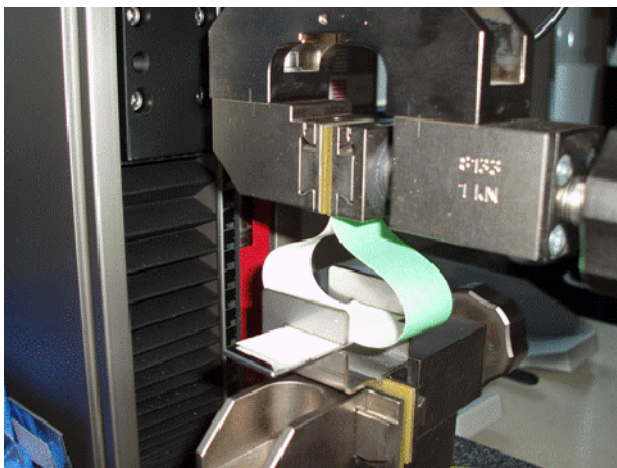


Figure 3. Loop tack on paper according to AFERA 4015.

In summation, the tack of a pressure-sensitive adhesive can be considered to be primarily a measure of the wettability of that adhesive under controlled application conditions, with due regard for its optimum adhesion value. Tack increases continuously upon adding soft, viscous components to the formulation. To determine the tack property, various testing methods are suggested, for example, rolling ball tack test, quick stick tack test, probe tack test, and loop tack test (Figure 3) [15].

The loop tack test is widely used in the adhesive tape and PSA industries, primarily as a quality control tool. The test methods can be divided into two different types depending on which substrate the adhesive coats. In one, the adhesive is on the forming loop. This test is used to test adhesive tapes. In the other, the adhesive is on the rigid base plate. This test method tends to be used for double-sided tapes, pressure sensitive adhesives, and coatings. The most popular method is the AFERA Test Method 4015.

### ***1.3.2 Peel adhesion***

The characteristic feature of PSAs is that they form a permanently tacky film after evaporation of the liquid phase of a solution or dispersion, or after cooling of a melt, or after the reaction of a 100 per cent solid system. This permits the production of self-adhesive products, a potential that is being utilized in many different ways.

The adhesion to the substrate to be bonded is the actual purpose of PSAs applying. In the first phase, when the PSA contacts the substrate under a light pressure, a bond is formed. First of all, only small, individual adhesion points are formed, but during the contact phase, the number and size of these points are increased by elastic deformation, viscous flow, and wetting of the substrate by the adhesive. The second phase includes the separation of the assembly by means of a tension force. The assembly is deformed in the process.

High peel adhesion requires certain tack level for bonding and certain cohesion for debonding. The dependence of the peel on the ratio of elastic/viscous components is more complex, going through a maximum as a function of the level of the soft component [14].

There are two meanings of the term "adhesion". On the one hand, adhesion is understood as the process through which two bodies are attached to each other when brought together. In this sense adhesion characterizes the sum of all intermolecular and electrostatic forces acting across the interface. On the other hand, we may examine the process of breaking the already adhesive in contact. In this case adhesion is the force, or the energy, required to separate the two bodies, often called "practical adhesion" or "adherence".

One would believe that in describing the adhesion of a pressure-sensitive adhesive in the form of tapes it would be a measure of the force that holds that pressure-sensitive adhesive tape to an applied surface. In fact, though, it is actually a measure of the force required to remove it from that surface. Removal involves work done in extension of the adhesive, the work done in distorting the

backing during the stripping action, and the work done in separating the adhesive/surface interface, the last being the smallest of the three [16].

According to ASTM (American Society for Testing Materials), adhesion is "a state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking action, or both". A theoretical treatment of adhesion in terms of intermolecular interaction is not just confined to bond energies; other important factors are the number of contact points of the interacting atoms or molecules, intermolecular distances, the mobility of atomic groups and the structure of neighboring matter.

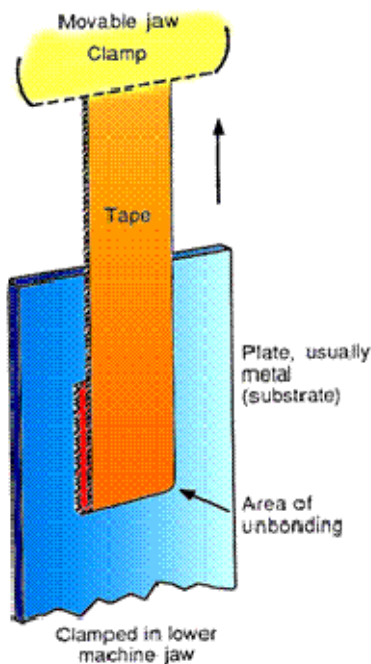


Figure 4. Peel adhesion test.

Many theoretical models of adhesion have been proposed, which together are both complementary and contradictory. The most important will now be: mechanical interlocking, adsorption (or thermodynamic) theory, electrostatic theory, chemical bonding theory, diffusion theory of adhesion, adhesive effect of thin liquid films and theory of weak boundary layers [17]. Each of these theories of adhesion is supported by experimental analysis but for each there are also convincing counter arguments.

The measurement of peel adhesion of PSAs is illustrated in Figure 4.

### ***1.3.3 Adhesion-cohesion Balance***

Pressure-sensitive adhesives possess adhesion, required for bonding and debonding, and cohesion necessary against debonding. Adhesion is characterized by tack and peel, whereas cohesion is described by shear resistance, and partially by peel. The special balance of these properties, the adhesion/cohesion balance, embodies the pressure-sensitive character of the adhesive. The efficiency of the bonding process is related to the adhesive's ability to exhibit viscous flow. In order to achieve peel adhesion the bonding stage involves some dwell time. During this time the adhesive must flow in the absence of any externally applied forces. The more liquid-like the behavior of the polymer under these conditions, the more pronounced the degree of bond formation. The debonding process involves a more rapid deformation of the adhesive mass. The polymer's resistance to deformation at higher strain rates becomes very important; the higher this resistance, the higher the force which must be applied to separate the adhesive from the adherent (i.e. the peel resistance). Therefore, high tack, high peel strength adhesives should exhibit good flow at low strain rates, but good resistance to flow at higher strain rates [18].

A proper balance between high tack, peel adhesion, and high cohesion is necessary in most cases. The behavior of any pressure-sensitive adhesive can be reduced to three fundamental and interconnected physical properties: tack, adhesion (peel adhesion), and shear resistance (cohesion). A clear understanding of each property and term is essential.

### ***1.3.4 Shear strength***

The most important means to influence the shear strength (cohesion) of PSAs are tackification and crosslinking. Pressure-sensitive adhesives possess typical visco-elastic properties, which allow them to respond to both a bonding and a debonding step. For permanent adhesives the most important step is the debonding one; the adhesive should not break under debonding (mainly shear and peel) forces (i.e., permanent adhesives must provide a higher level of cohesive or shear strength than removable adhesives).

When an increasing shear force is applied to a pressure-sensitive adhesive tape that has been applied to a surface, initially trapezoidal distortion of the adhesion takes place. Eventually a point will be reached when tape failure results. The nature of that failure is dependent on how quickly the liquid component of the adhesive can respond to the applied force. At one end of the spectrum, with a high stress or a rapidly increasing stress, the behavior will be largely elastic and the adhesive will separate at the interface leaving a trace of adhesive residue, or the tape backing will break. At the other end of the spectrum, the liquid component of

the adhesion can respond fully, allowing molecular disentanglement within the adhesive resulting in cohesive failure (Figure 5).

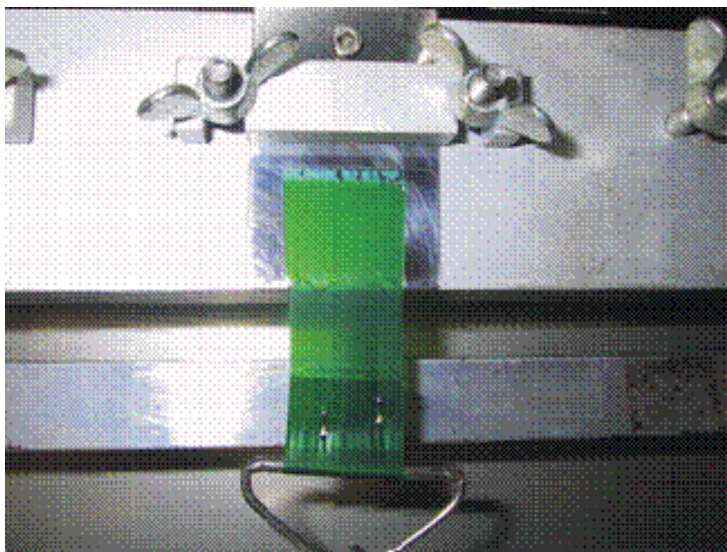


Figure 5. Shear strength test.

Typical shear resistance testing is performed with a controlled area of adhesive tape (pressure-sensitive adhesive layer) applied to a standard test surface. Because shear failure is the inability of the pressure-sensitive adhesive to resist a continuous stress, any task that is a measure of stress relaxation within the adhesive gives meaningful data. A high shear resistant adhesive will maintain the stress, while a poor shear resistant adhesive will relieve the stress quite rapidly [19].

### ***1.3.5 Shrinkage***

Although acrylic polymers have been used successfully as pressure-sensitive adhesives in a variety of industries, a property inherent to all acrylic PSAs, which negatively impacts adhesion performance is shrinkage on PVC surfaces upon crosslinking. This phenomenon is attributed to the formation of a three-dimensional, covalently crosslinked network during crosslinking, which reduces intermolecular distances between the monomers used to form the crosslinked network. Before cure, the molecules which comprise the resin are separated by

their characteristic van der Waal's radii. Upon cure, these intermolecular distances are reduced due to the formation of covalent bonds between monomers which produce the desired highly crosslinked thermoset material. This reduction of intermolecular distances creates internal stress throughout the thermoset network, which is manifested by reduced adhesion of the thermoset material to both the substrate and the object attached thereto.

Before crosslinking, the molecules, which comprise the PSA acrylate are separated by their characteristic van der Waals radii. Upon crosslinking, these intermolecular distances are reduced due to the formation of covalent bonds between monomers which produces the desired highly crosslinked PSA material. This reduction of intermolecular distances creates internal stress throughout the crosslinked network, which is manifested by reduced adhesion of the PSA adhesive to both the substrate and the object attached thereto.

Shrinkage presents the percentage or millimeter change of dimensions of the PVC foil covered with PSA after PSA crosslinking and attached to the glass after keeping it 1 week at temperature of 70°C. With shrinkage greater than 0,5 % or greater than 0.5 mm other properties were neglected (Figure 6) [20].

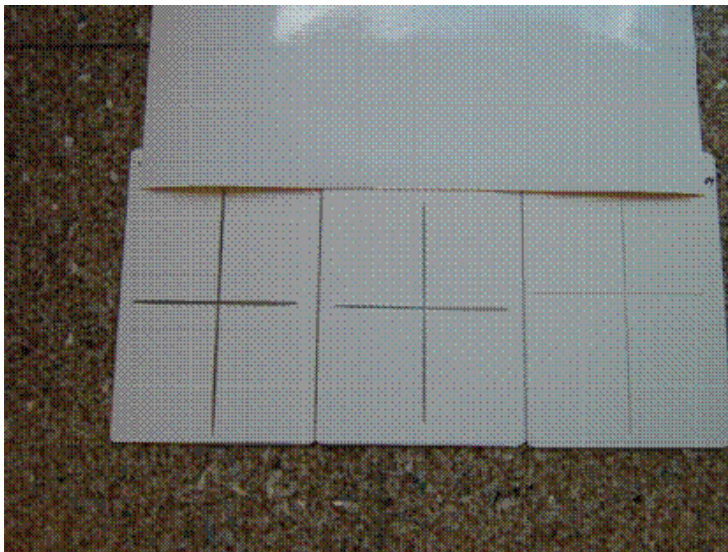


Figure 6. Measurement of PSAs shrinkage.

### ***1.3.6 Other Important Properties***

In general, a pressure-sensitive adhesive product consists of a component that provides adhesivity, which is the PSA and the carrier that provides desired

mechanical properties. Some products can be carrier-free. In addition, pressure-sensitive products can include a release liner, which is one side or both sides siliconized. The other significant properties of polymeric PSAs, depending on industrially application, are important by following characteristics:

- Thermal resistance
- Plasticizer resistance
- Water resistance
- Removability and responsibility
- Water-solubility
- Photoreactivity

## 2. APPLICATIONS OF PRESSURE-SENSITIVE OF ADHESIVES

Pressure sensitive adhesives (PSAs) are widely used polymeric materials in our modern life, such as in one-sided, double-sided or transfer mounting tapes, sign and marking films, self-adhesive labels, masking tapes, protective films, packaging tapes, in the automotive and machine industry, air space, building and electronic industry, the shoe industry, and medical applications.

Pressure-sensitive adhesives are applied from solvent solutions, water dispersions or solvent-free systems. After that, they form a permanent tacky film after the evaporation of the solvent or weather phase or after cooling of a hot-melt. Bonding is affected by slightly pressing the adhesive surface onto the adherend. These three groups can demonstrate different properties and characteristics (Table 1).

Solvent-borne adhesives are synthesized in solvent and are coated onto a web. Following coating, the solvent evaporates, leaving a functional adhesive. Solvent-borne PSA acrylics offer several advantages such as excellent aging characteristics and resistance to elevated temperatures and plasticizers, exceptional optical clarity due to the polymer compatibility and non-yellowing. They also have the highest balance of adhesion and cohesion and an excellent water resistance. The numerous advantages of solvent-based acrylic PSA have led to their wide use in the manufacture of self-adhesive products.

**Table 1. Properties and characteristic of pressure-sensitive adhesives [21]**

| Property          | Solvent-borne PSAs                                                            | Water-borne PSAs                                                                        | Solvent-free PSAs                                                         |
|-------------------|-------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------|---------------------------------------------------------------------------|
| Solid content, %  | 20–50                                                                         | 40–69                                                                                   | 100                                                                       |
| Drying rate       | Usually fast, drying time adjustable by choice of solvents                    | Slow to dry; however, high solids content meant less to dry                             | No volatiles to evaporate                                                 |
| Surface wet-out   | Excellent on most surfaces, even without minor contamination                  | Good on porous substrates, poor to fair on non polar surfaces like plastics             | Good on most surfaces, may require heating the surface before application |
| Water resistance  | Usually good to excellent                                                     | Fair to good                                                                            | Excellent                                                                 |
| Temperature range | –55 to 160°C                                                                  | –40 to 120°C                                                                            | –45 to 140°C                                                              |
| Surface attack    | May cause degradation of some plastic and paint                               | Causes shrinkage and wrinkling of fabric and paper; corrosive to metal                  | Usually no problem; heat may deform thin plastics                         |
| Flexibility       | Excellent                                                                     | Excellent                                                                               | Excellent                                                                 |
| Hazards           | Requires vapour control; many are flammable and many require emission control | Usually no problem; some have trace levels of chemicals that require control of vapours | Few problems other than working with hot dispensing equipment             |
| Cleanup           | Solvent                                                                       | Water when wet; solvent when dry                                                        | Solvent                                                                   |
| Cost              | Low to moderate cost per gallon; <i>high cost</i> per dry unit of weight      | Moderate cost per gallon; <i>low cost</i> per dry unit of weight                        | <i>Moderate cost</i> per dry unit of weight                               |

Solvent-free system and emulsion are two additional types of adhesives. Emulsion adhesive ingredients are polymerized in water, applied to the web and dried to create a functional adhesive. Solvent-free as hot-melt adhesives are made from thermoplastic rubbers that formulate with tackifying resins, oils, and antioxidants to achieve coating on the web at high temperatures. Solvent-free pressure-sensitive adhesives are relatively new group of self-adhesive technical and medical products and demonstrate many advantages in opposite to solvent-based pressure-sensitive adhesives. The main aspect is reduction of environmental impact to a minimum during production and exploitation.

Advantages and disadvantages of those three PSAs groups are presented in Table 2.

**Table 2. The advantages and limitations of solvent-borne, water-borne and hot-melt adhesives [22]**

| Pressure-sensitive adhesive | Advantage                            | Limitation                            |
|-----------------------------|--------------------------------------|---------------------------------------|
| Solvent-borne               | Quick drying                         | Flammability                          |
|                             | Form homogenous films                | Toxicity                              |
|                             | Good adhesion to non polar substrate | Relatively low solid content          |
|                             | Good key on certain plastics         | Difficult cleaning                    |
| Water-borne                 | Easy cleaning                        | Slow drying                           |
|                             | Good adhesion to polar substrates    | Require heat to dry                   |
|                             | Good heat and ageing resistance      | Poor adhesion on non polar substrates |
|                             | Environment friendly                 | Presence of surfactant                |
|                             | High solid content                   |                                       |
| Hot-melt                    | 100% active                          | High equipment costs                  |
|                             | Environment friendly                 | Require heat                          |
|                             | Very fast setting                    | Thermal degradation                   |
|                             |                                      | Difficult to clean                    |
|                             |                                      | Can melt the substrate                |

**2.1. Applications form of Pressure-Sensitive Adhesives**

In addition to a variety of carriers and adhesives, PSA manufacturers offer a range of pressure-sensitive products, which has different constructions. They are used as double-sided, one-sided and carrier-free (transfer) self-adhesive materials.

**2.1.1 Double-sided tapes**

Double-sided tapes are constructed from carrier, which is double-sided coated with pressure-sensitive adhesive. The PSA layers on carrier are protect using release liner in form of dehesive paper or polymeric film (Figure 7).

Copyright © 2011, Nova Science Publishers, Incorporated. All rights reserved.

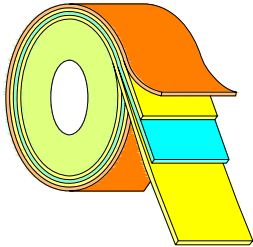
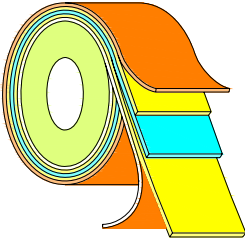
|                                                                                   |                                                                                   |                                                                                                              |                                                               |
|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------|
| <b>Double-coated tape</b>                                                         |  | Adhesive is coated on both sides of carrier material, and both sides siliconized release liner protect tape. | Self-adhesive gasketing and abrasive sanding/ polishing pads. |
| <b>Double-lined, double coated tape</b>                                           |  | Similar to double-coated PSP, but they have release liner one side siliconized on both sides.                | Die-cut parts and assembly aids or gaskets.                   |
|  |                                                                                   |                                                                                                              |                                                               |

Figure 7. Construction of double-sided PSA tapes.

2.1.2. One-sided tapes

One-sided tapes containing PSA layer coated directly on the carrier. The self-adhesive layer is protecting with carrier backing side coated with release (Figure 8).

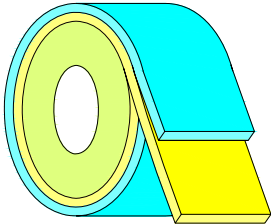
|                           |                                                                                     |                                                                                      |                                                  |
|---------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|--------------------------------------------------|
| <b>Single-coated tape</b> |  | Adhesive is coated on one side of a facestock and silicone coated on the other side. | Diapers, electrical, masking, and packing tapes. |
|---------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|--------------------------------------------------|

Figure 8. Construction of one-sided PSA tapes.

2.1.3 Carrier-free tapes

Carrier-free tapes other known as transfer tapes containing PSA layer protecting both-sided with backing coated with release agents (Figure 9).

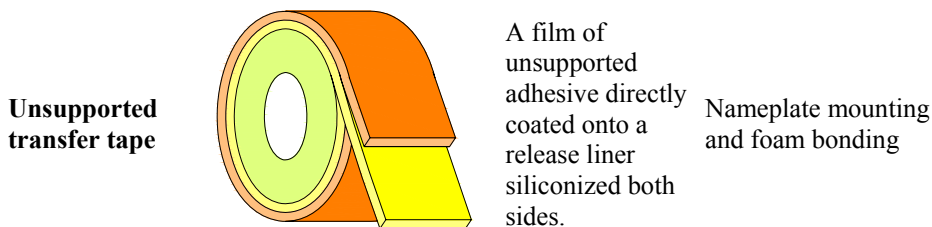


Figure 9. Construction of carrier-free PSA tapes.

## 2.2. Technical applications of self-adhesive products

Self-adhesive products are manufactured as double-, one-sided or carrier-free tapes applied in various fields of industrial applications. The most important are illustrated below.

### *Mounting Tapes*

Mounting tapes have been developed for a wide range of industrial applications. Thermal resistant acrylic mounting tapes maintain their performance characteristics up to 160-180°C and silicone tapes up to 280-300°C and adhere to a variety of surfaces including metals, glass, paper, wood, and plastic. They must exhibit good electrical properties and good resistance to chemicals, as well as to fungus, moisture, and weathering. Mounting tapes used in buildings must have the same expectancy as the building elements. Such mounting tapes can replace other classic mechanical methods of fixing. Foam-backed adhesive tapes are commonly used to adhere an article to a substrate. The foam carrier can be pigmented with carbon black or with titan dioxide, to camouflage the presence of the tape. A foam-like PSA tape is manufactured using glass microbubbles as filler. Dark glass microbubbles are embedded in a pigmented adhesive matrix. The average diameter of the microbubbles should be between 5 and 200  $\mu\text{m}$ . Optimum performance is attained if the thickness of the PSA layer exceeds seven times the average diameter of the bubbles.

### *Splicing Tapes*

Splicing tapes have been used in paper, converting, and printing industries. The adhesive and end-use requirements for splicing tapes are very severe. High tack and fast grabbing are required for high speed flying splicing. The tapes have to exhibit adhesion to various papers, liner board, foils, and films as well as high-

shear resistance and temperature resistance while traveling through drying oven. The application time for splicing tapes is very short, in many cases less than 60 s. Splicing tapes for the paper manufacturing have to be recyclable and resist temperatures up to 220-240°C. The main types of splicing tapes are one-side-coated tape, double-side-coated tape and transfer tape. Splicing tapes used in the paper manufacturing industry have to be tested for such important properties as tack and adhesion on paper, dynamic and static shear strength at room and high temperatures, resistance to greasing and bleed through, water solubility at pH 3, 7, 9 and 12. Special acrylic based composition from splicing tapes can change their adhesive properties as a function of the atmospheric humidity.

### ***Packaging Tapes***

The classic tape construction, a mechanically resistant nondeformable but flexible carrier material coated with high coating weight of an aggressive but inexpensive adhesive, is valid for packaging tapes without special requirements. The high processing speed for these tapes requires the decrease of the noise level. Packaging tapes are applied either by hand or by automatic packaging machines for the fastening of goods. Generally, packaging tapes are based on PVC or PP, and they may also have a reinforcing layer. Kraft paper, cloth and oriented plastic carrier material are also used. For packaging tapes on hot-melt PSAs basis, adhesion on card-board is of special importance and the main property is a combination of shear, peel adhesion and tack. Common PSA systems for packaging tapes are based on SIS rubbers.

### ***Insulating tapes***

There are insulating tapes used for a variety of applications, mainly for electrical or heat insulation or as a sealant. They must have excellent mechanical, electrical, and thermal properties. Wire-wound tapes, electrically conductive or electrically insulating tapes, and thermally insulating tapes are the most important representatives of this product class. They are used for taping generator motors and coils and transformers, where the tape serves as overwrap, layer insulation, or connection and lead-in tape. Insulating tapes with acetate carrier are used for wire winding by telephone manufactures. Typical insulating tapes are coated with conventional crosslinkable or UV-crosslinkable acrylic PSAs. Electrical tapes must be approved by Underwriter Laboratories and require elongation, shear, and peel resistance. Electrical tapes have to possess high dielectric strength and good dissipation properties.

### ***Electrically Conductive Tapes***

Generally, electrical conductivity is achieved using special conductive filler. Tapes with adequate electrical conductivity are made using a metal carrier (nickel foil) and an adhesive having nickel particles as filler. Electrically conductive tapes have been manufactured by coating an acrylic dispersion or solvent-borne systems containing nickel, aluminum, and silver or electrically conductive carbon blacks. Electrically conductive tapes containing carbon black are characterized by very good electrical properties, tack, peel adhesion and shear strength. Silver-coated glass powder or glass microbubbles as filler lead to a specific surface conductivity.

### ***Foam Tapes***

Classic foam tapes are foam-like materials with a foamed plastic carrier that is coated with PSAs. The foam carrier provides excellent conformability and stress distribution. In the typical applications, the PSA is coated first on a dehesive paper or film and then laminated onto the carrier surface. Foam sealing tapes are made of foam sealing tape layer and an interlayer strip rolled up together in a compressed form. For such tapes, there are standard thickness, roll lengths, and ranges of width given by the supplier. Special foam mounting tapes are used for bonding of soft printing plates for flexo printing. Foam tapes can compensate for tolerances in the printing process and assure that dot gain is minimized. Automotive insert tapes are used as sealants. Such products are tapes based on a foam carrier and have to exhibit aging stability, weatherability, sealing, and nonflammability.

### ***Transfer Tapes***

Transfer tapes, other known as carrier-free tapes, are tapes without carrier. The sheet backing is a release liner, and in use, the exposed adhesive surface of this tape is placed in contact with a desired substrate, the release liner stripped away, and the newly exposed adhesive surface bonded to the second surface. Their construction includes a release liner and the adhesive core. Transfer tapes have been developed about a decade ago. They can be used for structural bonding. Transfer tapes for structural and semistructural bonding have such relevant properties as high temperature resistance, good environmental resistance, conformability to the substrate shape, and low and constant adhesive thickness and variable adhesive thickness. The transfer process of the tape from the temporary liner can be regulated by means of the release, but it can also be controlled by using different adhesives having different degrees of crosslinking. The radiation-curable compositions and curing procedure can also be used for

transfer tape. Glass microbubbles can be incorporated also in order to enhance immediate adhesion to rough and uneven surfaces.

## 2.3 MEDICAL APPLICATIONS OF SELF-ADHESIVE PRODUCTS

Medical instruments, equipment or products with short-term contact include syringes, cannulas, catheters, valves, filters, respiratory masks, keyhole surgery instruments, endoscopes and orthodontic aids. These are composed of very different materials that sometimes are difficult to bond, such as metal alloys of aluminum, medical steel, titanium, nickel, or plastics such as polyethylene (PE), polypropylene (PP), polycarbonate (PC), or oxidic materials as glasses and ceramics. Acrylic systems are used for the manufacturing of sterile disposable products and orthopedic devices.

Self-adhesive products such as band-aids are the most ancient and popular applications of adhesives in the medical sector. PSA tapes come into contact with the human body for several days, while acrylic spray-on adhesives are widely used on cleansed wounds where they replace band-aids.

Surgical, PSA sheet products include any product that has a flexible carrier material and a PSA. Medical labels, tapes, adhesive bandages, adhesive plasters, adhesive surgical sheets, adhesive corn plaster, and adhesive absorbent dressings have been manufactured. Medical tapes have been developed for pharmaceutical companies, ostomy appliances, diagnostic apparatus, surgical grounding pads, transdermal drug delivery systems, and wound care products.

Physiologically compatible adhesives are based on acrylic, silicones, polyvinyl ether, polyester and polyurethanes. They minimize skin irritation due to their ability to transmit air and moisture through the adhesive system. New ways are opened by use of antiviral agents as fillers for the carrier or the adhesive. For medical tape adhesives are required skin tolerance, no physiological effects, resistance to skin humidity, and sterilizing capability without color changes.

Surgical tapes are used for fastening cover materials during surgery. Cotton cloth and hydrophobic special textile materials coated with low energy polyfluorocarbon resins are used as carriers and coated with special acrylic formulations. Preferred carrier materials are those that permit transpiration and perspiration or the passage of tissue or wound exudates therethrough. They should have a moisture vapor transmission of at least  $500 \text{ g/m}^2$  over 24 h at  $38^\circ\text{C}$  with a humidity differential of at least about  $1000 \text{ g/m}^2$ .

For medical tapes rubber-based and acrylic homo- and copolymers have been used. For a composition containing polar comonomers with built-in, containing

carboxyl or hydroxyl groups, comonomers with crosslinking properties have been used. The pressure-sensitive adhesives used for medical application in form of medical products are sterilized with ethylene oxide or gamma radiation. After sterilization they have to adhere to skin, wet textiles, and nonwovens [1].

## REFERENCES

- [1] I. Benedek, “*Developments in Pressure-Sensitive Products*”, Ed. by Istvan Benedek, Taylor & Francis a CRC Press Book, New York (2006).
- [2] Z. Czech, A. Butwin, Replacement of UV-crosslinkable acrylic pressure-sensitive adhesives hotmelts by warmmelts and low viscosity systems cotable at room temperature, 35. Munich Adhesives and Finishing Symposium, Munich (2010) 167-177.
- [3] R. Milker, Z. Czech, A. Butwin, Photoreactive acrylic pressure-sensitive adhesive hotmelts, their synthesis, properties and applications, 35. Munich Adhesives and Finishing Symposium, Munich (2010) 235-244.
- [4] Z. Czech, *Crosslinking of pressure-sensitive adhesives based on acrylics*, Ed. by Szczecin University of Technology, Szczecin (1999).
- [5] Z. Czech, A. Butwin, B. Hefczyc, J. Zawadiak, *Polimery* 4 (2009) 283-287.
- [6] Z. Czech, A. Butwin, E. Herko, *Coating International* 8 (2008) 22-25.
- [7] P. Kröger, W. Schimmel, Haftklebstoffe auf Acrylatbasi, 9. Munich Adhesives and Finishing Symposium, Munich, Germany (1984) 76-83.
- [8] X. Jin, Y. P. Bai, L. Shao, B. H. Yang, Y. P. Tang, *eXPRESS Polymer Letters*, 12 (2009) 814-820.
- [9] Z. Czech, A. Butwin, K. Zych, *European Coatings Journal*, 3 (2009) 90-95.
- [10] Y. P. Bai, L. Zhao, L. Shao, *Journal of Applied Polymer Science*, 115 (2010) 1125-1130.
- [11] Z. Czech, *International Journal of Adhesion and Adhesives*, 27 (2007) 49-58.
- [12] Z. Czech, R. Milker, A. Butwin, E. Herko, *Polish Journal of Chemical Technology*, 2 (2008) 37-40.
- [13] I. Benedek, *Pressure-Sensitive Design and Formulation, Application*, Ed. By VSP, Vol. 2, Leiden, (2006).
- [14] Z. Czech, A. Kowalski, J. Ortyl, “Tack of pressure-sensitive adhesives (PSAs), *Coating* 1 (2011) 1-4.
- [15] Y. Woo, Dissertation, *Inelastic analysis of the loop tack test for pressure sensitive adhesives*, September (2002), Blacksburg, Virginia.
- [16] W. Druschke, Adhesion and tack of pressure-sensitive adhesives, AFERA

- meeting, October, Edinburgh, (1986) 1-12.
- [17] O. Aydin, A. Dragon, "*Pressure-Sensitive Adhesives*", *Coating Handbook*, BASF, Germany (2001).
  - [18] I. Benedek, L. J. Heymans, "*Pressure-Sensitive Adhesives Technology*", Marcel Dekker Inc., New York, USA (1997).
  - [19] R. Milker, Z. Czech, UV and Thermal Crosslinkable Solvent-Free Acrylic PSA Systems, Pressure Sensitive Tape Council TECH XXVIII Technical Seminar, Baltimore, USA, Mai, (2005) 239-258.
  - [20] R. Milker, Z. Czech, Solvent-Based PSA Acrylics with low shrinkage and high performance, Conference AFERA, Haga, Holland, (2004) 151-165.
  - [21] Petrie, E. M., Adhesive classification, In *Handbook of Adhesives and Sealants*, McGraw-Hill. USA (2000).
  - [22] Goulding, T.M., Pressure-sensitive adhesives, In *Handbook of adhesive technology 1*. Marcel Dekker, New York (1994).



### *Chapter 3*

## **ELECTRICALLY CONDUCTIVE ADHESIVES BASED ON EPOXY RESINS REINFORCED WITH CARBON NANOFILLERS**

***Silvia G. Prolongo, María R. Gude and Alejandro Ureña***

Department of Materials Science and Engineering,  
Universidad Rey Juan Carlos, c/Tulipán s/n, Móstoles, 28933, Madrid (Spain)

### **ABSTRACT**

The present chapter is a review of the most relevant experimental results obtained for the development of conductive nanoreinforced adhesives. The epoxy adhesives are filled with low loadings of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) in order to increase widely their electrical conductivity, remaining their adhesive ability and even improving their mechanical and thermal behaviour. Taking into account their possible applications as structural adhesives, the adhesive strength and toughness of the joints was measured using lightweight adherends, as carbon fiber/epoxy laminates, which are commonly used in the aerospace and automobile industries.

The critical stage of the manufacturing process of nanoreinforced adhesives is the dispersion of the nanofillers. A dispersion procedure based on the use of an organic solvent was optimised to reach suitable dispersion degrees at low carbon nanofiller contents (< 0.5 wt.%). High nanofiller concentrations had to be rejected due to the excessive increase of the adhesive viscosity.

The addition of CNFs and CNTs was probed to induce a light increase of the maximum use temperature of the adhesive and an important improvement of their tensile mechanical properties. The lap shear strength is not affected by the presence of the nanofillers while the joint toughness, measured by double cantilever beam test, significantly increases. It was probed that both properties strongly depend on the surface pre-treatment applied to the laminate adherends. Also, nanoreinforced epoxy adhesives show high electrical conductivity, allowing the dissipation of electrostatic charges when conductive adherends are joined.

## INTRODUCTION

The electrically conductive adhesives (ECAs) mainly consist on a polymer matrix reinforced with metal-conductor fillers. In general, the conductive fillers provide the electrical properties while the polymer matrices provide the physical and mechanical properties [1]. The electrical resistivity of an ECA must be lower than  $10^8 \Omega \cdot \text{cm}$  in order to be able to dissipate static charges [2]. There are different kinds of ECAs as function of the size of conductive filler (Figure 1): a) anisotropically conductive adhesive (ACA) based on adhesive film with a typical 3-5  $\mu\text{m}$  sized conductive fillers and b) isotropically conductive adhesives (ICA) formed by an adhesive with 1-10  $\mu\text{m}$  sized fillers. Until now, the conductive fillers used usually were metallic particles with micro-scale size: silver, gold, nickel and copper. Different carbon fillers have been also used in various sizes and shapes.

Silver flakes are the most commonly used conductive fillers for commercial ICAs due to the high electrical conductivity, simple process, maximum contact with flakes, high chemical resistance and even its corresponding oxide also is conductor. Oxides of most common metals are generally good electrical insulators. Nickel and copper have low resistance stability because they are easily oxidized. Therefore, the antioxidants addition is necessary to the adhesive formulations [3].

The so-called percolation theory is generally used to describe the transition from insulating polymer to electrical conductor. Composites containing conductor fillers in insulating polymers become electrically conductive when the filler content exceeds a critical value, known as the percolation threshold. The percolation threshold is characterised by a sharp jump in the conductivity of many orders of magnitude and it is attributed to the formation of the three-dimensional conductive network of the filler within the matrix. Its value depends on the shape and size of the fillers, but it is typically in the order of 15-25 % volume fraction

for the traditional ECAs. Moreover, for ICA, the filler loading level usually exceeds the percolation threshold in order to provide electrical conductivity in all three space directions.

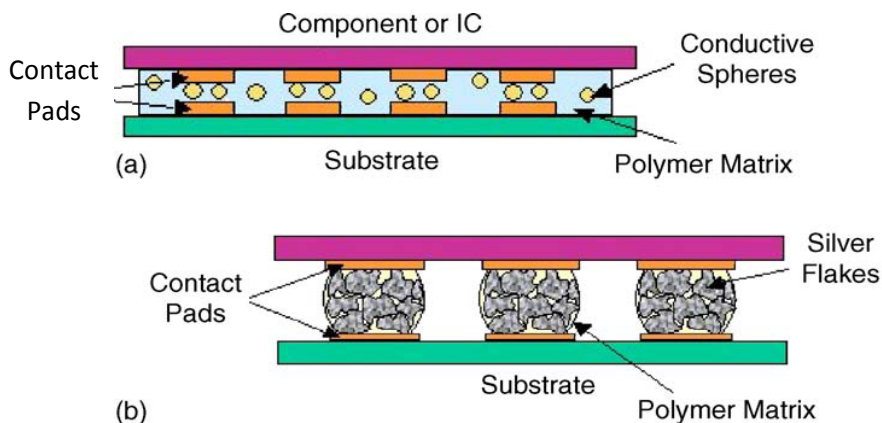


Figure 1. Schematic illustration of a) ACA and b) ICA.

Recently, a new type of conductive fillers is being researched based on conductive nano-sized fillers, such as carbon nanotubes and carbon nanofibers. The advantages of nano-sized fillers are numerous. One of them is their very high surface area which causes that the percolation threshold is very low, typically lower than 0.1 %. The addition of some nanoreinforcement can also improve other properties of the adhesive, such as its mechanical properties, thermal resistance and even thermal conductivity. Besides, it is expected that the addition of nano-sized fillers increases the adhesion force in the adhesive/adherend interface associated to new mechanisms of mechanical nano-scale anchorage [4-6].

In this review, the study is centred on the epoxy adhesives reinforced with CNTs and CNFs. Epoxy adhesives are the most common used structural bi-component adhesives with high thermal and chemical resistance. The main drawbacks of the epoxy adhesives are their low toughness, low electrical resistivity and relative high water absorption ability in humid environments. In some cases, the high electrical resistivity of epoxy adhesives could be beneficial, i.e. the joint of insulator materials. However, for the joint of metal-conductor materials, it is necessary to increase their conductivity in order to keep the electrical behaviour on the bonded structure.

In this way, one of the most interesting possible applications could be the joining of carbon fiber/epoxy laminates. These materials are increasingly used in the aerospace industry where the size, shape and design of the some components usually require the use of joints between several pieces. The structural components of aircrafts must be electrically conductors in order to be able to dissipate charges associated to the possible lightning strike. Therefore, the development of an electrically conductive adhesive based on an epoxy resin with improved adhesive, mechanical and thermal properties would be very useful.

In spite of the numerous researches published about epoxy nanocomposites reinforced with CNTs and CNFs, few works have been found related with their application as adhesives. Hsiao et al. [6] reported increases of 31 and 46 % in the lap shear strength values of carbon fiber/epoxy laminates joints when the epoxy adhesives were reinforced with 1 and 5 wt.% CNTs, respectively. These improvements were associated to the effective load transfer from the nanotubes of the adhesive to carbon fiber of the adherends, which was probed by the observed damage on the fibers of the substrate of the broken joints surfaces. So, the failure mode changes from adhesive mode for the joints bonded with non-modified epoxy adhesive to cohesive mode (break through the laminate adherends) for ones bonded with nanoreinforced adhesives.

On the other hand, Meguid and Sun [7] probed that the addition of CNTs increases the joint strength. Higher nanotube contents imply higher strength up to a maximum value close to 2.5 wt.%. From this value, the joint properties fall down. CNTs could fill voids and porosities, increasing the contact points and improving the adhesion. Additional contents would imply the formation of agglomerates which would act as stress concentrators.

The present work collects a review of the most relevant results obtained in the study of epoxy adhesives reinforced with CNTs and CNFs. First, it is necessary to carry out the optimization of the manufacturing process of the nanoreinforced adhesives. Particularly, the dispersion degree reached is critical in order to achieve the best properties of the nanocomposite. Also, the rheological behaviour of the non-cured mixtures is analyzed. It is known that the nanofillers addition usually induces important increases on the viscosity of samples, which would hinder their application as adhesives. The mechanical and thermal properties of epoxy nanocomposites have been determined. Finally, their adhesive behavior has been analyzed and the strength and toughness of the joints, using carbon fiber/epoxy laminates adherends, has been measured.

## PROCESSING OF NANOREINFORCED ADHESIVES

As discussed above, the addition of carbon nanofillers into epoxy adhesives is a critical stage in the manufacture of nanoreinforced adhesives. In order to achieve optimal improvement in the properties of the nanofilled adhesives, the obtaining of suitable carbon nanofillers dispersion is the main key to be resolved. Especially, for the development of ECA, the highly electrical conductive carbon nanofillers must form a three-dimensional conductive network of the nanofiller within the matrix [8-10].

The dispersion degree reached strongly depends on the concentration, nature, aspect ratio and functionalization of nanofiller and over all on the different dispersion techniques applied. CNTs and CNFs are generally entangled in the form of curved agglomerates, produced for the synthesis and caused by the strong intermolecular van der Waals forces. Therefore, their dispersion is usually complex. There are several techniques to improve the dispersion of carbon nanofillers in polymer matrices: optimum physical blending, in situ polymerization and chemical functionalization. The high power dispersion methods, such as ultrasound and high speed shearing, are the simplest and most convenient to disperse nanofillers in thermosetting matrixes. In addition, the surfaces of nanotubes can be chemically functionalized to achieve good dispersion in nanocomposites and strong interface adhesion between surrounding polymer chains, even though the interface area is very large. A strong large interface generally improves the load transfer from the matrix to the nanoreinforcements, increasing the mechanical properties of the nanocomposite [10-12].

Through the implementation of several consecutive works [13-15], the authors have optimized a dispersion method based on sequential stages, using chloroform as solvent and several physical dispersion techniques: magnetic stirring, ultrasonication and shear mixing. The influence of several parameters, such as the use and nature of solvent, the stirring temperature, the functionalization of nanofiller between others, was analysed. Figure 2 shows optical micrographs of the non-cured adhesives as function of the experimental conditions applied during the dispersion procedure.

One of the most relevant stages of our optimized dispersion procedure is the last one, before the addition of hardener, which consists on the application of thermal treatment to the mixture formed by epoxy prepolymer with dispersed functionalized nanotubes. The objective of the named pre-curing thermal treatment is to induce the chemical reaction between epoxy monomer and amine-functionalized nanofiller.

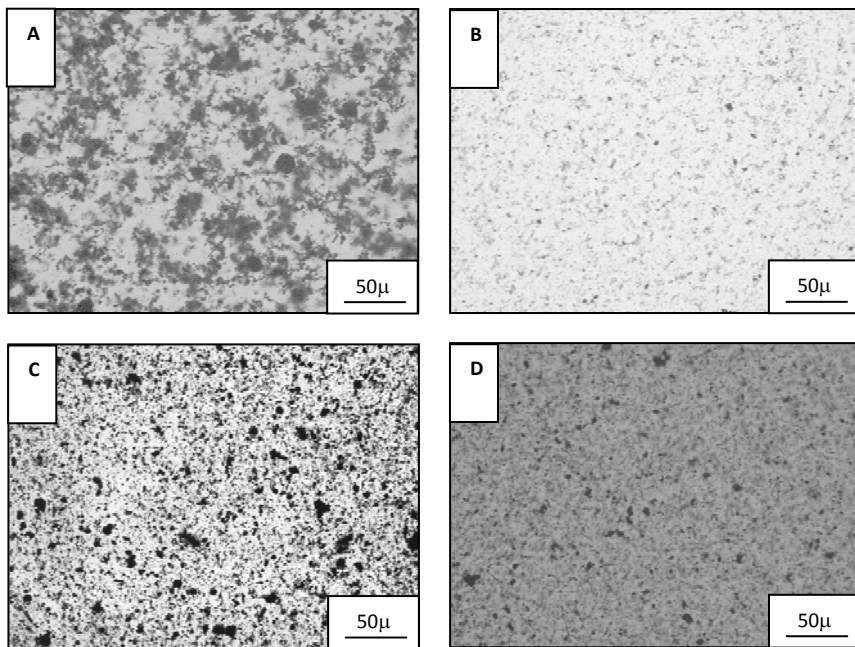


Figure 2. Transmission optical micrographs showing different dispersion methods: A) without solvent, B) diluted in chloroform, C) only magnetic stirring and D) diluted in chloroform with magnetic stirring, ultrasonication and shear mixing.

The dispersion degree reached on the pre-cured samples is better than the non-treated ones (Figure 3). The absent of large agglomerates in the pre-cured samples confirms the enhancement of dispersion due to the thermal pre-curing treatment and also that this improved dispersion is stabilised and maintained after the epoxy adhesive is fully cured. Long nanotubes are pulled out from the matrix when the samples were not pre-cured (micrograph C). In contrast, the pull-out nanotubes are very short in a small number on pre-cured composites (micrograph D). This indicates the formation of a stronger bond between the matrix and CNTs due to the thermal pre-curing treatment. As it is schematically indicated in the figure 4, in the pre-cured nanocomposite (scheme B), the failure has propagated across the whole section, which is named fracture mode of the weakest link. It is known that this only occurs when the filler is very strongly bonded to the matrix and the matrix is very brittle, such the epoxy resin. In contrast, the non-precured sample shows longer nanotubes over the fracture surface due to debonding and filler pull out, indicating a weaker interface (scheme A) [16].

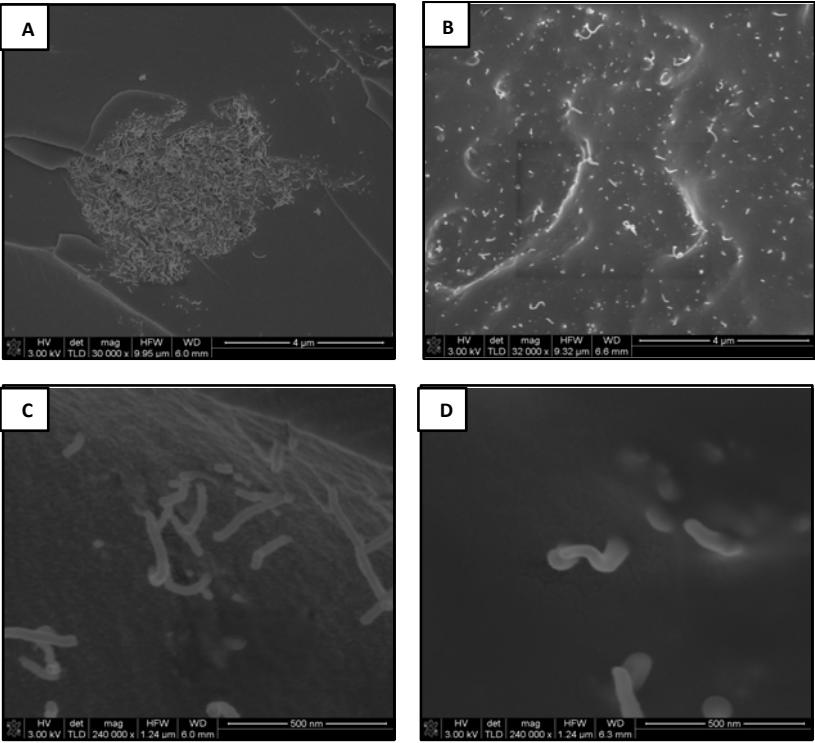


Figure 3. Micrographs, captured by high-resolution scanning electron microscopy, of cured epoxy nanocomposites manufactured without (A,C) and applying the pre-curing thermal treatment (B,D).

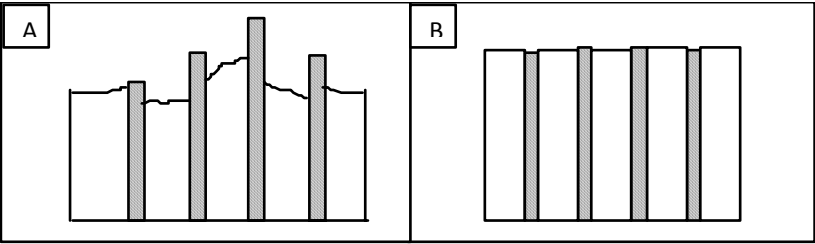


Figure 4. Schematic representations of fracture surface: A) Fibrous surface due to debonding and fibre pull-out and B) planar fracture. The dispersion degree reached on the nanocomposite manufacture has a wide influence on the properties of material. In fact, a poor dispersion and rope-like entanglement of CNTs and CNFs led to drastic weakening of the composites. However, a well dispersed nanocomposite presents improved properties compared with the ones of neat epoxy resin. The thermal, mechanical and electrical properties are increased by the addition of carbon nanofillers.

**Table 1. Mechanical properties of epoxy adhesives reinforced with CNTs and CNFs.**

| Property                | Epoxy matrix | Nanofiller           | Content (wt.%) | Value       | Increment (%) |
|-------------------------|--------------|----------------------|----------------|-------------|---------------|
| Flexural strength (MPa) | DGEBA/DDS    | -                    | 0              | 98 ± 4      |               |
|                         |              | NH <sub>2</sub> -CNT | 0.25           | 155 ± 3     | 58            |
|                         |              | NH <sub>2</sub> -CNT | 0.40           | 131 ± 4     | 34            |
|                         | DGEBA/DDM    | -                    | 0              | 99 ± 22     |               |
|                         |              | NH <sub>2</sub> -CNT | 0.1            | 93 ± 11     | -6            |
|                         |              | NH <sub>2</sub> -CNT | 0.25           | 106 ± 7     | 7             |
|                         |              | CNF                  | 0.25           | 130 ± 10    | 40            |
|                         |              | CNF                  | 0.5            | 107 ± 15    | 8             |
| Flexural strain (%)     | DGEBA/DDS    | -                    | 0              | 3.4 ± 0.1   |               |
|                         |              | NH <sub>2</sub> -CNT | 0.25           | 5.7 ± 0.7   | 68            |
|                         |              | NH <sub>2</sub> -CNT | 0.40           | 4.4 ± 0.2   | 29            |
|                         | DGEBA/DDM    | -                    | 0              | 5.8 ± 1.5   |               |
|                         |              | NH <sub>2</sub> -CNT | 0.1            | 6.5 ± 1.0   | 12            |
|                         |              | NH <sub>2</sub> -CNT | 0.25           | 6.6 ± 0.3   | 13            |
|                         |              | CNF                  | 0.25           | 6.2 ± 0.9   | 7             |
|                         |              | CNF                  | 0.5            | 6.6 ± 0.7   | 14            |
| Young Modulus (GPa)     | DGEBA/DDS    | -                    | 0              | 3.37 ± 0.16 |               |
|                         |              | NH <sub>2</sub> -CNT | 0.25           | 3.29 ± 0.12 | -2            |
|                         |              | NH <sub>2</sub> -CNT | 0.40           | 3.63 ± 0.09 | 11            |
|                         | DGEBA/DDM    | -                    | 0              | 2.62 ± 0.07 |               |
|                         |              | NH <sub>2</sub> -CNT | 0.1            | 2.46 ± 0.06 | -6            |
|                         |              | NH <sub>2</sub> -CNT | 0.25           | 2.62 ± 0.16 | 0             |
|                         |              | CNF                  | 0.25           | 3.23 ± 0.06 | 23            |
|                         |              | CNF                  | 0.5            | 2.60 ± 0.09 | 0             |

Table 1. collects the mechanical properties of the nanocomposites with two different epoxy adhesives. Both are based on diglycidyl ether of bisphenol A (DGEBA) as epoxy monomer cured with two different aromatic amine hardeners. In the most of cases, the addition of carbon nanofillers causes an important increase of the mechanical strength and flexural strain. Even, the stiffness (measured by elastic modulus) seems to increase regard to the neat epoxy

adhesive. All these increases should necessarily imply an increase of the toughness [17].

This is a special quality of 2D-nanofiller, as CNTs and CNFs. The traditional micro-sized fillers usually improve some mechanical properties at the expense of others. For example, the epoxy adhesives reinforced with micro-sized thermoplastic or rubber particles present important increases of their deformation ability and toughness at expense of a drastic fall of their modulus. On the other hand, the epoxy composites reinforced with traditional carbon fibers present high mechanical strength and stiffness but low strain. This particularity of the nanocomposites is associated to the special characteristics of the nanofibers and nanotubes. These nanoreinforcements have spectacular mechanical properties, with an elastic modulus close to 1 TPa and with values of mechanical strength around 10 – 60 GPa. Moreover, carbon nanofillers present very high aspect ratio and highly flexible elastic behaviour during load, which are very different to micrometer-size fibers. Additionally, the curved nanotubes and nanofibers are typically twisted and entangled and can therefore continuously stretched. This behaviour contributes to continuous absorption of energy and results in increased strain in the epoxy thermoset [18].

The nature of the epoxy adhesive affects to the final mechanical properties of the nanocomposite. In fact, it seems that the addition of carbon nanofillers gives higher flexibility to the most crosslinked epoxy resin (DGEBA/DDS), which initially was the most stiff (with lower strain and higher modulus). So, the addition of 0.25-0.40 wt.% CNTs induces increases up to 68 % in the flexural strain and up to 11 % in the elastic modulus. The mechanical strength increases up to 40 – 58 % independently of the used epoxy adhesive.

The nature of the nanoreinforcement seems also to affect to the obtained improvements. Except to the elastic modulus, the higher increases of mechanical strength and strain are reached by the nanocomposites reinforced with carbon nanotubes. This is the expected since the mechanical properties of the CNTs are usually higher than the ones of CNFs.

Finally, the nanofiller content also influences the final properties of the nanocomposites. Regarding carbon nanotubes, it seems that there is a maximum optimum content of CNTs (0.25 wt.%), higher loadings imply a fall of the properties. This is associated to the high surface area of carbon nanotubes and their high tendency to agglomerate. High CNTs contents cause the appearance of agglomerations, which can act as stress concentrations, hindering a good mechanical behaviour of nanocomposite.

## RHEOLOGICAL BEHAVIOR

One of the disadvantages of the nanofillers addition into epoxy adhesives is the high increase of their viscosity, which can reduce their wettability. It has been probed that better nanofiller dispersion induces higher increases of the non-cured mixtures viscosity. Therefore, it is necessary to carry out a study of the viscosity of mixtures formed by epoxy monomer and different contents of nanofillers as a function of the temperature. Figure 5 shows the obtained results.

The viscosity of the mixtures increases with the addition of nanofillers [19-22]. For the same content of carbon nanofiller, the mixture viscosity is much higher with CNT than with CNF, which could be associated to higher specific surface area (close to 300 m<sup>2</sup>/g for CNTs and 150 – 200 g/m<sup>2</sup> for CNFs), and to the better dispersion of CNTs. At high CNT content, the thermal pre-curing treatment causes an important viscosity increase likely due to the chemical reaction between epoxy and amine-functionalized CNTs.

The relationship between viscosity and temperature does not seem to depend on the nanofiller content or its nature and it can be described by Arrhenius equation. There were found two different slopes in the Arrhenius plot. At low temperature (below 45 °C), the activation energy is higher. The ratio between the activation energies at low and high temperature is in range from 1.3 to 2.5, indicating that near room temperature the decrease of viscosity with the temperature is more marked. This behaviour indicates that the lack of free volume is the dominant mechanism at temperature close to the glass transition temperature ( $T_g$  of epoxy monomer is -17°C, measured by differential scanning calorimetry) [23]. The values of the activation energies are higher for the epoxy mixtures reinforced with CNT and over all, when these mixtures are precured. The activation energies for non-reinforced adhesive are 136 and 75 kJ/mol, for low and high temperature range. In contrast, the values obtained for the mixture with 3 % CNFs are 111 and 54 kJ/mol, respectively.

## WETTABILITY

As it was commented above, the main application of these electrically-conductor epoxy adhesives could be the aerospace industry, which requires structural adhesives with high thermal and chemical strength, high adhesive strength and toughness, together with the ability to charge dissipation. When lightning strikes an airplane, generated electric power must be dissipated to avoid

damage to the structure. Therefore, the joints can not be electrically insulators. Currently, the tendency of the new aircraft designs is increasingly the use of composites materials. For it, the wettability of the nanoreinforced adhesives over adherends of carbon fiber/epoxy laminates is studied [24,25].

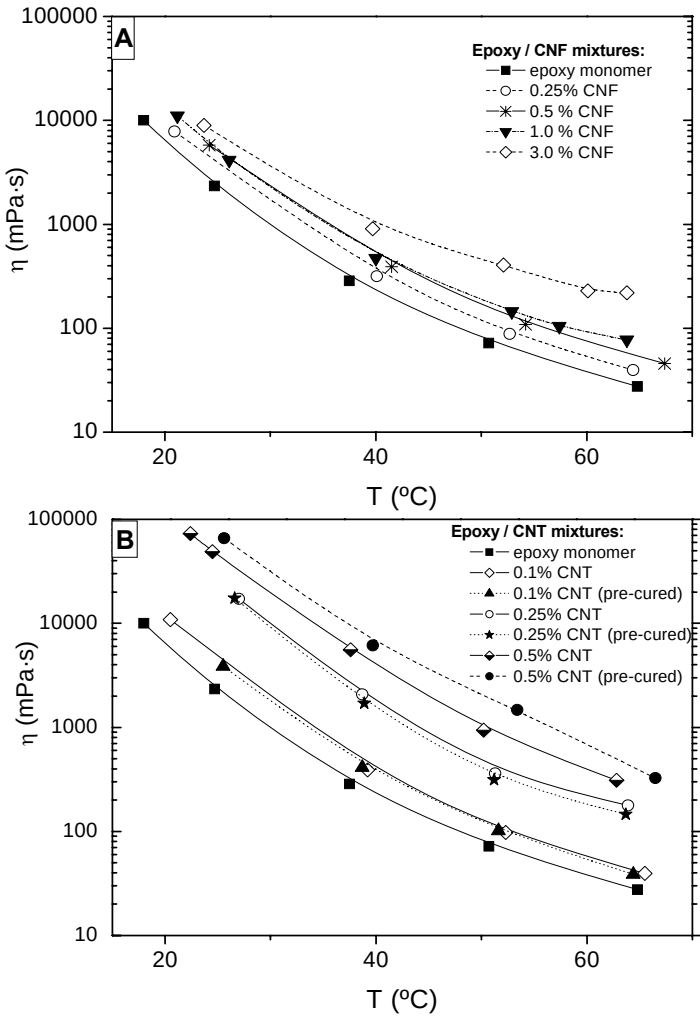


Figure 5. Rheological behaviour of non-cured epoxy mixtures reinforced with different contents of CNFs and amine-CNTs.

Joining surfaces must present surface properties which promote the adhesion. This requires the application of surface treatments, especially in the case of low surface energy materials, like polymer matrix composites. The surface treatments must modify the chemistry and morphology of a thin surface layer without affecting the bulk properties. In general, the aims of surface treatments are i) to remove any weak boundary layer on the surface of the adherend, such as contaminants, oxidized layers or low molecular weight species, which can be the origin of adhesive failure of the joint, ii) to improve wetting of the adhesive over the adherend, iii) chemical modification such as the introduction of different chemical groups into the surface which can form acid-base or stronger primary bonds with the adhesive and iv) to increase the surface roughness, giving rise to improved mechanical interlocking or increased bondable surface area [26].

The effectiveness of any surface treatment is dependent upon the type of substrate and the extent of the treatment. There is a wide variety of surface treatments. The most common used for composites materials of polymer matrix are grit blasting, peel ply and plasma. Grit blasting is the simplest surface treatment to improve adhesion. It modifies the surface morphology, increasing the roughness and therefore the effective surface area, promoting the mechanical interlocking. Also, it removes the surface contamination. Peel ply treatment is one of the most used surface treatments in the composite industry, due to its low cost and ease to use. It consists on a single ply placed on one side of composite material prior to the manufacturing process. During the cure cycle, this ply is progressively impregnated with the polymer matrix of the composite, remaining as fully part of the composite. Then, its removing leads to a rough surface, which is the negative of the peel ply used, increasing the surface free energy. However, the peel ply usually leaves rest of release agents on the surface of adherends. Plasma surface treatment is another common technique for composite materials, where the adherend surface is exposed to ionized gas, usually generated by radio frequency energy. The plasma region contains a high concentration of reactive species, such as ions and electrons, which are formed from the gas. Various studies have indicated that these energetic species interact with the surface and cause chemical and texture changes. Some researchers have found that plasma treatment increases the concentration of polar groups on the surface.

Figure 6 collects the contact angle of a pristine epoxy adhesive and the reinforced ones with different contents of carbon nanofibers. The contact angle decreases with the nanofiller addition which is explained by the nano-scale size of the nanofiber and the higher chemical compatibility between carbon fiber/epoxy composite and nanoreinforced epoxy adhesive. However, the increase of CNFs percentage added causes an increase of contact angle although the measured value

is lower than that of neat epoxy adhesive in the most cases, except to the epoxy adhesive reinforced with 1 wt.%. This increase could be associated to the worse dispersion of the nanofiller when its content is higher, possibly forming agglomerations of CNFs which increase its effective size.

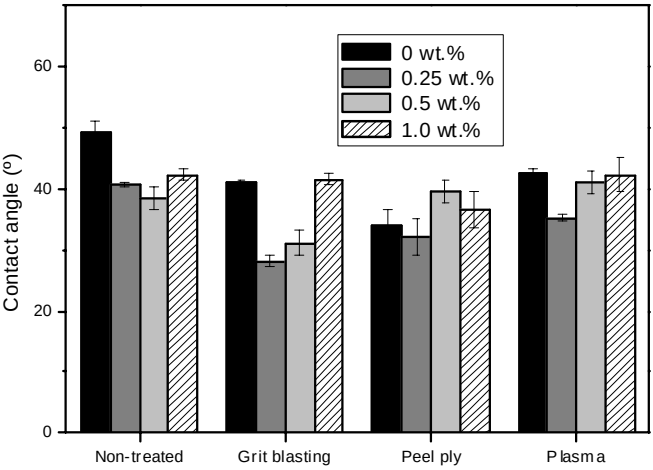


Figure 6. Contact angle of neat epoxy adhesive and CNFs reinforced epoxy adhesives on carbon fiber/epoxy laminates (non-treated and treated with grit blasting, peel ply and plasma).

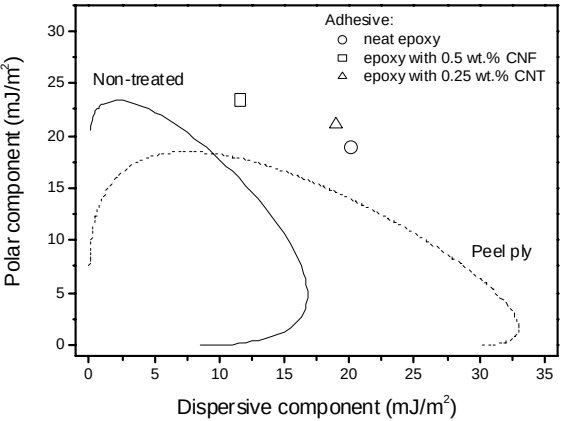


Figure 7. Wetting envelope of the non-treated and peel ply treated adherends and surface tension of the neat epoxy adhesive and reinforced with 0.25 wt.% CNTs and 0.5 wt.% CNFs.

The wetting envelopes represent the polar and dispersive fractions of the surface tension of a liquid which wets the surface with a given contact angle. For  $0^\circ$ , this curve represents the critical surface tension for complete wetting. For different surface finishes, the wettability is better when the liquid is closer to the wetting envelope. Figure 7 shows the wetting envelope of non-treated and peel ply treated adherends and surface tension of the neat epoxy adhesives and reinforced ones with 0.25 % CNTs and CNFs. The three adhesives have similar behaviour, in spite of the lower contact angle of nanoreinforced adhesives.

On the other hand, it is confirmed that for the laminates treated by peel ply the adhesives wet better the surface than for non-treated adherends. This is the result expected, because the surface free energy of the peel ply treated laminates is higher. However, it may be observed that liquids with certain combinations of the components of surface tension (high polar, low dispersive component) will wet better the non-treated laminates. This fact indicates that wetting depends not only on the surface free energy of the adherend and the surface tension of the liquid but also on how the dispersive and polar components of both are distributed.

## ADHESIVE STRENGTH AND TOUGHNESS

The adhesive strength of neat epoxy and nanoreinforced resins was determined by single lap shear test following the standard ASTM D5868, using the carbon fiber/epoxy laminate adherends treated by plasma, grit blasting and peel ply (Figure 8). It is observed that the addition of CNFs scarcely affects to adhesive strength in spite of the angle contact decreased (Figure 6), improving the wettability of the nanoreinforced adhesives. This could be associated with the presence of defects in the nanoreinforced adhesives, such as voids generated by the evaporation of remaining chloroform during the thermal curing treatment applied to the adhesive. This solvent is used to disperse carbon nanofibers into epoxy monomer and it probably was not rightly removed before joining.

The measured lap shear strength strongly depends on the surface treatment applied to the composite. The highest strength is obtained for the composite treated by plasma due to the higher surface energy of these surfaces. The relative high adhesive strength of the joints with grit blasted adherends could be related to the increase of roughness generated. Peel ply treatment gives low values of lap shear strength. It has been reported that peel ply treatment based on polyester tissue leads to a decrease of mechanical performance, mainly as the consequence of a decrease of chemical adhesion between the adhesive and adherent due to the contamination with silicone. The failure mode depends on the applied surface

treatments. While the break of joints with peel ply treated adherends was totally adhesive, the fracture of plasma treated ones was partially cohesive in the adherends and in the case of grit blasted composites, their joints broke cohesively in the adherend. These observations are consistent with the measured lap shear strength. While the CNF loading scarcely affects (Figure 8), the nature of the added nanofiller (CNT and CNF) significantly affects to the joint strength and it is different as function of the surface pre-treatment applied to the adherends (Figure 9).

A study carried out by scanning electron microscopy at very high magnifications over the fracture surfaces of non-modified and nanoreinforced epoxy adhesives shows significant differences between them. Contrarily to the case of the neat epoxy adhesive, where damage is characterized by the presence of small and poorly developed shear cusps, well developed and plastically deformed shear cusps were observed in the case of the nanoreinforced epoxy adhesive, in the joint with grit blasted and plasma treated adherends. A higher proportion of river markings and microflow was also found on cusp surfaces formed from mode II crack propagation across the nanoreinforced adhesive. Observation at higher magnification (Figure 10) showed the roll played by CNFs in the crack propagation and final formation of shear cusps.

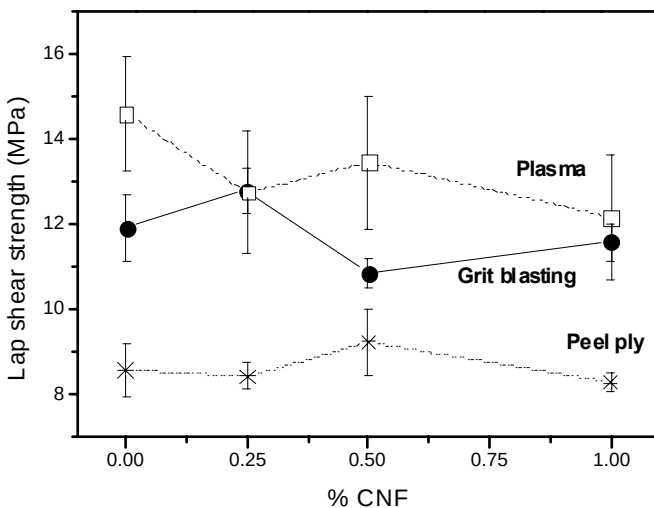


Figure 8. Lap shear strength of neat epoxy adhesive and reinforced ones with different contents of CNFs, using carbon fiber/epoxy laminates, treated with grit blasting, peel ply and plasma, as adherends.

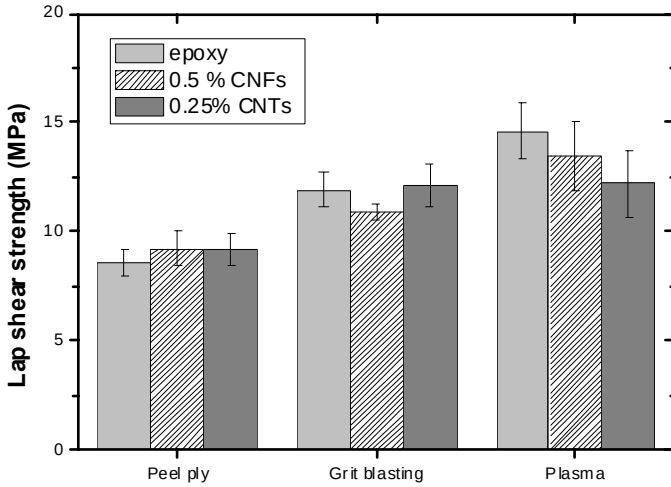


Figure 9. Lap shear strength of neat epoxy adhesive and reinforced ones with 0.5 wt.% CNFs and with 0.25 wt.% CNTs, using carbon fiber/epoxy laminates, treated with grit blasting, peel ply and plasma, as adherends.

Small voids with sizes in the range of the nanofiber diameters found on surfaces of the cusps could show the participation of these carbon nanofibers in pull-out mechanisms from the adhesive matrix. The shear sliding of those CNFs oriented on the fracture plane (white arrowed in Fig. 10b) favour the matrix deformation in mode II.

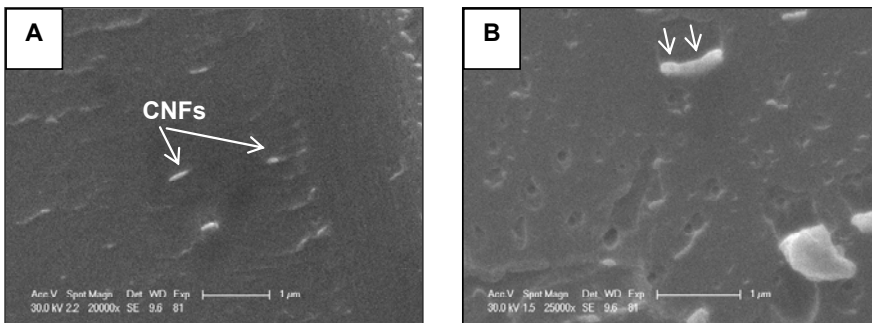


Figure 10. SEM micrographs at high magnifications of joints whose adherends were treated by plasma (failure mode: mixed adhesive-cohesive) and whose adhesive was epoxy resin reinforced with 0.5 wt.% CNFs.

The joint toughness can be analysed through the mode-I adhesive fracture energy ( $G_{Ic}$ ), using double cantilever beam joints. Figure 11 shows the  $G_{Ic}$  values obtained for the joints of carbon fiber/epoxy laminates treated by peel ply using a neat epoxy and nanoreinforced adhesives with 0.25 wt.% CNTs and 0.5 wt.% CNFs. For each DCB tested joint, three calculation methods were applied: Area method (Area), Corrected beam theory (CBT) and Experimental compliance method (ECM). Although the standard deviation is quite high in some cases, in general, the mean values of each adhesive are very similar, independently of the method used for the calculation.

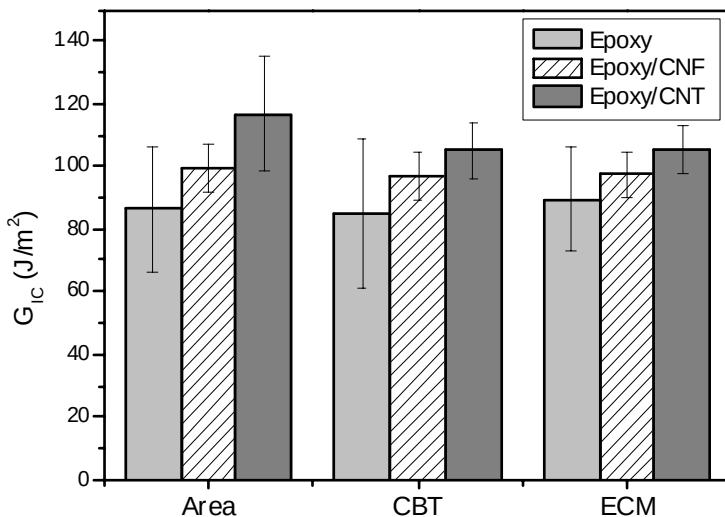


Figure 11.  $G_{Ic}$  values obtained for the joints of carbon fiber/epoxy laminates treated by peel ply using a neat epoxy and nanoreinforced adhesives with 0.5 % CNFs and 0.25 % CNTs. Comparison of the mean propagation values and standard deviation of  $G_{Ic}$  as a function of the calculation method.

The mode-I fracture energy of DCB joints increases by the addition of carbon nanoreinforcements. The reinforcement of epoxy adhesives with CNFs increases the mode-I fracture energy of DCB joints of carbon fiber/epoxy laminates in 10 % with regard to the neat adhesive, while the increase with CNTs is 23.5 %. This is in total agreement with the previous results reported about the mechanical properties of the nanocomposites reinforced with CNTs and CNFs. As it is expected, carbon nanotube is better reinforcement than carbon nanofiber.

In all the tested joints with neat and CNF reinforced adhesive, the failure was found macroscopically adhesive while the samples bonded with CNT/epoxy adhesive broke in a mixed mode adhesive/cohesive in the adhesive. In these last joints, the crack moves from an adhesive/adherend interface to the opposite, and also propagates through the adhesive layer. This could indicate that carbon nanotubes improve the interface between adhesive and substrates, preventing the crack propagating along it and causing the “stick-slip” crack growth behaviour. This gives rise to an increase of the mode-I adhesive fracture energy.

The observation of fracture surfaces at high magnification shows clear differences. The neat adhesive showed flat surfaces with practically total absence of fibrillation, which means very low energy consumption during crack propagation. In the nanoreinforced adhesives, there are zones of microcohesive failure, increasing the participation of fibrillation micromechanisms, which are promoted by the presence of CNFs and CNTs. In fact, for CNT/epoxy nanocomposite, which provides better adhesive fracture energy, the presence of new micro-mechanical mechanisms, such as crack bridging or CNT pull out are observed (Fig. 12). This toughening mechanism explains the higher values of  $G_{IC}$  calculated for the adhesive reinforced with CNTs, compared with neat adhesive.

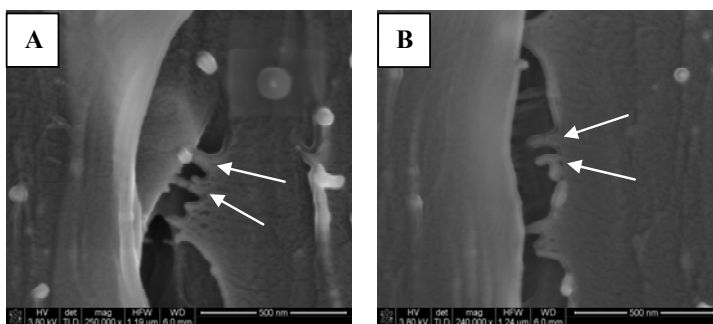


Figure 12. High resolution micrographs showing the participation of CNTs, pointed with white arrows, A) bridging and B) pull-out micro-mechanisms.

## ELECTRICAL PROPERTIES

As mentioned above, numerous applications require the joint of metal-conductor materials, therefore, it is necessary to use an ECA to keep the electrical continuity. The electrical resistivity of an ECA must be, at least, lower than  $10^8 \Omega \cdot \text{cm}$  in order to be able to dissipate static charges and, more favourable, lower

$10^3 \Omega\cdot\text{cm}$  in order to be able to electromagnetic shielding properties [1]. Taking into account the electrical resistivity of neat epoxy adhesives is close to  $10^{15} \Omega\cdot\text{cm}$ , this parameter must be drastically decrease. The carbon nanofillers are characterised for their high electrical conductivity, in the order of  $10^3 \text{ S}\cdot\text{cm}$ , depending on their nature (CNTs and CNFs), number of walls of CNTs, functionalization, etc.

Figure 13 shows the effect of the addition of CNT and CNF on the electrical resistivity of the epoxy nanocomposites. The epoxy resin modified with both CNT and CNF presents similar behaviour in terms of the electrical resistivity versus content of nanofiller as the electrical resistivity drastically decreases by increasing the nanofiller loading. The electrical resistivity is decreased in several orders of magnitude, depending on the nature of the nanofiller. At high nanofiller contents, the electrical resistivity remains approximately constant and it seems that the appearance of large agglomerates of CNF does not affect to this property.

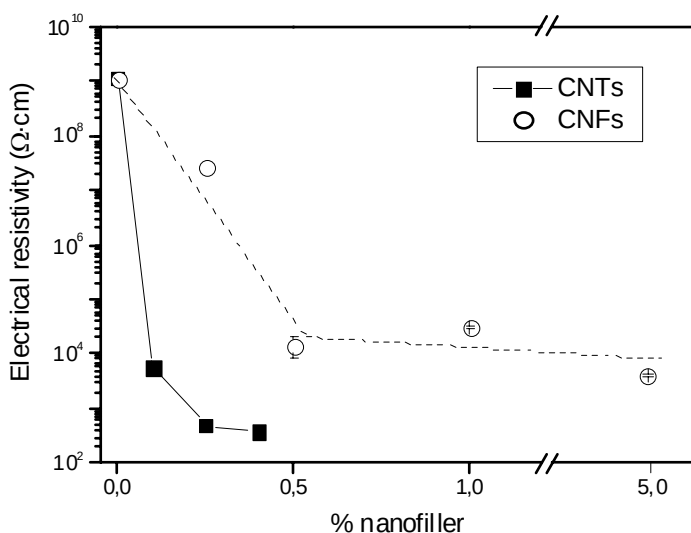


Figure 13. Electrical resistivity of epoxy adhesives reinforced with CNTs and CNFs.

The epoxy resin reinforced with CNT and CNF exhibit low percolation threshold for electrical conductivity, lower than 0.5 wt.% nanofiller. This very low value is explained by the large aspect ratio and the nano-scale dimensions of the nanofillers. In fact, the electrical resistivity of the epoxy resin reinforced with CNT is two orders of magnitude lower than the one of epoxy/CNF composites

because of the different structure, the higher aspect ratio ( $\sim 1000$  for CNTs and  $\sim 300$  for CNFs) and higher surface area of CNTs ( $\sim 300 \text{ m}^2/\text{g}$  for CNTs and  $\sim 175 \text{ m}^2/\text{g}$  for CNFs). The traditional polymer reinforced with micro-sized particles present similar behaviour. Figure 14 shows the effect of filler aspect ratio on the critical filler concentration needed to induce bulk conductivity in a filled polymer [27].

The values of electrical resistivity obtained for the nanofilled adhesives are similar than the reported for other authors for epoxy resins reinforced with CNTs ( $10^4 - 10^2 \text{ } \Omega \cdot \text{cm}$ ), manufactured with different dispersion techniques. This may indicate that the dispersion degree reached by the nanofiller within the epoxy matrix is not a critical parameter, as it was concluded above. This is right at relative high CNT contents regard to the percolation threshold. It is known that the dispersion degree affects to the value of this threshold, being lower, the higher dispersion degree is.

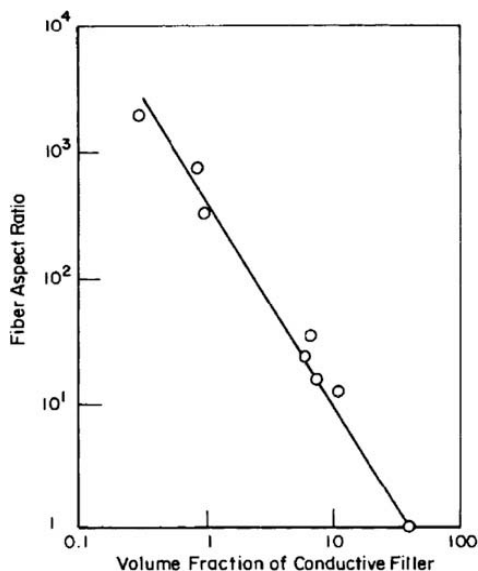


Figure 14. Effect of the filler aspect ratio on the percolation threshold for conventional micro-sized filled polymers.

The high electrical conductivity of the nanoreinforced epoxy adhesives is of great interest for application as adhesive of carbon fiber/epoxy laminates. In fact, the values of electrical resistivity for the nanoreinforced epoxy adhesives are similar than the one of the carbon fiber/epoxy laminates. Therefore, the joint of

these materials with carbon nanofiller adhesives would present a uniform electrical behaviour, being very similar to that of the complete structure.

It is worthy to note that the values of electrical resistivity of nanocomposites are lower than the necessary ones to dissipate electrical static charges. Moreover, the electrical resistivity measured for epoxy adhesives reinforced with CNTs shows that they would have electromagnetic shielding properties. On the other hand, it is necessary to indicate that the electrical resistivity reported for other ECAs (ie. adhesives reinforced with silver particles) are much lower than the obtained for the nanofiller adhesives, close to  $10^{-3}$ – $10^{-4}$   $\Omega$ -cm. The reason is the very high loading level added, around 15-20 % [1]. The applications of the adhesives reinforced with traditional metal particles are associated to joint metallic adherends in electrical devices, but their mechanical and even adhesive requirements are much lower than the found ones for nanofiller adhesives.

## CONCLUSIONS

The nanofilled adhesives based on the addition of carbon nanofibers and nanotubes are an interesting and promising alternative to manufacture electrically conductive adhesives. However, there is still much research in this field in order to achieve a commercial application. The main advantages of nanofilled adhesives regard to the conventional electrically conductive adhesives are the wide enhancements on the mechanical and thermal properties. The increase of the joint toughness is especially useful, remaining their strength. It is worthy to stand out the very low loading values used, lower than 1% in weight, which implies low modification of the wettability and viscosity of the non-cured adhesives. Also, in spite of the relative high price of the carbon nanofillers, actually their increasing use in numerous industrial applications and the low contents added to the nanofilled adhesives could remain competitive prizes of the final electrically conductive adhesives compared to conventional ECAs with 15-20% metal particles, such as silver.

The main efforts on the researches related to nanofilled adhesives will have to guide in the objective to increase their electrical resistivity in order to achieve values close to the ECAs. This is especially necessary to join metal adherends, remaining their electrical integrity. The electrical conductivity of some carbon nanotubes is very high, even higher than the noble metals. The problem is located on reaching a high dispersion degree in order to get total connectivity.

## REFERENCES

- [1] Y. Li, C. P. Wong. *Materials Science and Engineering* R51, 1, 2006.
- [2] J. Liu editor. *Conductive adhesives for electronic packaing*, electrochemical publications Ltd, British Isles, 1999.
- [3] J. Lau, C.P. Wong, N.C. Lee, S.W.R. Lee. *Electronics manufacturing: with Lead-free, Halogen-free and conductive adhesive materials*. McGraw Hill, New York, 2002.
- [4] C. A. Martin, J.K.W. Sandler, M.S.P. Shaffer, M.K. Schawarz, W. Bauhofer, K. Schulte and A. H. Windle. *J. Compos Mater* 64, 2309, 2004.
- [5] M. Moniruzzaman, K.I. Winey. *Macromolecules* 39, 1562, 2006
- [6] K. T. Hsiao, J. Alms, S.G. Advani. *Nanotechnology*, 14, 791, 2003.
- [7] S. A. Meguid, Y. Sun, Y. *Materials and Design*, 25, 289, 2004.
- [8] X. L. Xiea, B. Y. W. Maia, X. P. Zhou. *Materials Science and Engineering* R 49, 89, 2005.
- [9] N. Grossiord, J. Loos, O. Regev, C. E. Koning. *Chemical Materials* 18, 1089, 2006.
- [10] D. R. Paul, L. M. Roberson. *Polymer* 49, 3187, 2008.
- [11] L. S. Scahdler, S. C. Giannaris, P. M. Ajayan. *Applied Physics Letters* 73, 3842, 1998.
- [12] E. T. Thostenson, C. Li, T. W. Chou. *Composites Science and Technology* 65, 491, 2005.
- [13] S. G. Prolongo, M. Burón, M. R. Gude, R. Chaos-Morán, M. Campo, A. Ureña. *Composites Science and Technology* 68, 2722, 2008.
- [14] R. Chaos – Morán, M. Campo, S. G. Prolongo, M. D. Escalera, A. Ureña. *Journal of materials research* 24, 1435, 2009.
- [15] S. G. Prolongo, M. Campo, M. R. Gude, R. Chaos–Morán, A. Ureña. *Composites Science and Technology* 69, 349, 2009.
- [16] D. Hull. *An Introduction to composite materials*. Cambridge Soled State Science Series, USA, 1981.
- [17] S.G. Prolongo, M.R. Gude, A. Ureña *Composites Science and Technology*, 2011. (In press doi:10.1016/j.compscitech.2011.01.028).
- [18] J. N. Coleman, U. Khan, W. J. Blau, Y. K. Gun'ko. *Carbon* 44, 1624, 2006.
- [19] S. G. Prolongo, M. R. Gude, A. Ureña. *Journal of Nanoscience and Nanotechnology* 9, 1, 2009
- [20] S. G. Prolongo, M. R. Gude, A. Ureña. *Journal of Nanotechnology* 2010 (In press doi:10.1155/2010/420432).

- 
- [21] S. G. Prolongo, M. R. Gude, J. Sanchez, A. Ureña. *Journal of Adhesion* 85, 180, 2009.
  - [22] S. G. Prolongo, M. R. Gude, A. Ureña. *Journal of Adhesion Science and Technology* 24, 1097 (2010).
  - [23] Y. H. Hyun, S. T. Lim, H. J. Choi, M. S. John. *Macromolecules* 34, 8084, 2001.
  - [24] M. R. Gude, S. G. Prolongo, T. Gomez-del Rio, A. Ureña. *International Journal of Adhesion and Adhesives* (In press 2011)
  - [25] S. G. Prolongo, M. R. Gude, G. Del Rosario, A. Ureña. *International Journal of Adhesion and Adhesives* 24, 1855, 2010.
  - [26] J. R. J. Wingfield. *International Journal of Adhesion and Adhesives* 13, 3, 1993.
  - [27] D.M. Bigg. *Advances in Polymer Technology* 4, 255-266 (1984).



## ***Chapter 4***

# **ANTI-ADHESIVE LAYER FOR NANOIMPRINT LITHOGRAPHY**

***Jing Zhang, Weimin Zhou, Yanbo Liu, Jinhe Wang  
and Yanping Zhang***

Shanghai Nanotechnology Promotion Center, Shanghai, 200237

## **ABSTRACT**

Nanoimprint lithography is a method of fabricating nano-scale patterns with low cost, high throughput and high resolution. However, during nanoimprint lithography process, adhesion between the resist and the mold is one of the very factors which has affected the imprinted nanopatterns. As a result, improving anti-sticking properties of the stamps for nanoimprint lithography was intensively developed. In this chapter, the history and fabrication methods of anti-adhesive layer are reviewed in detail. Especially, we had developed a novel method of anti-adhesively self-assembled film by vapor phase deposition. Finally, personal remark is briefly ended with some views on the development of anti-adhesive layers.

## **1. INTRODUCTION**

Nanoimprint Lithography (NIL) is a very useful technique for the fabrication of nanoscale patterns. It was first reported by Stephen Chou in 1995 with the critical dimensions of sub-25nm [1]. On account of the advantage of low cost,

high-throughput and high resolution of patterning, it has attracted much attention in both academic research and industrial development [2-10]. And it has been added to the International Technology Roadmap for Semiconductors (ITRS) as one of the candidates for the 22, 16 and 11 nm nodes [11].

Though it is simple and of high resolution capability, NIL in its original form was not without problems and limitations. The sticking of the cured resist to stamp is the common problem during the demolding process in NIL, because of the large surface contact area and high shear force between polymer and stamp.

In this chapter, we begin with brief introduction of Nanoimprint Lithography in section 2, and then followed the mechanism of the sticking in section 3. The fabrication methods of anti-adhesive layer are reviewed in detail in section 4. In this section we especially introduce a novel method of anti-adhesive self-assembled film by vapor phase deposition developed in our laboratory. The chapter ends with a summary and future prospect.

## **2. THERMAL PRESS NANOIMPRINT AND UV NANOIMPRINT LITHOGRAPHY**

Nanoimprint is a simple way to fabricate nanostructure by replication of the stamp, like the manufacturing of the compact disks. Soon after its invention, many different types of NILs were promptly developed, and two of them are most important: thermal press nanoimprint (Hot Embossing) and UV nanoimprint lithography. The imprint lithography process is schematically outlined in Figure 1.

Thermal press nanoimprint was the first proposed NIL technology at nanometer scale. In this process, a thin layer of polymer is coated onto a flat substrate. Then the resist on the substrate is heated to about 50°C–100°C above its glass transition temperature ( $T_g$ ) so that the polymer is molten. A stamp with relief structures is imprinted into the resist film under certain pressure. After cooling under the resist's  $T_g$ , the stamp is separated from the polymer lay while the resist is still soft (demolding). After the demolding the reverse pattern keeps in the polymer layer. Next, a pattern transfer process (such as RIE, ICP) is followed to transfer the imprint pattern in the resist to the underneath substrate.

UV nanoimprint is based on a low viscosity, photocurable liquid and a UV transparent template. The low viscosity of the photocurable liquid eliminates the need of high temperature and pressures. The cavity of the stamp can be easily filled with the resist with a small applied pressure at the room temperature. After

exposure to the UV light, the photopolymer cures immediately. Therefore, UV-NIL allows a rapid production of nanoscale structures in a simple and parallel process. More importantly, the transparency of rigid stamp enables alignments during NIL process, hence realizing the overlay of NIL technology and the fabrication of integrated devices.

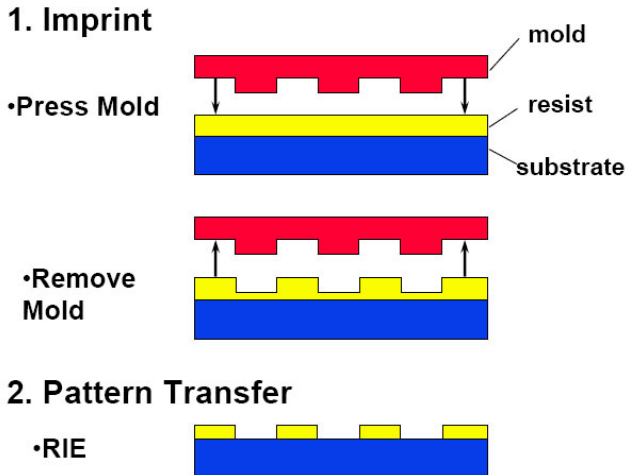


Figure 1. Schematic illustrations for nanoimprint lithography [12].

### 3. MECHANISMS OF ADHESION IN NIL [13-14]

There are several critical technologies in the nanoimprint lithography, such as the fabrication and treatment of the mold, the imprint resist, the defect of patterns, overlay of devices, and three demensionsal imprint patterns. One of the most critical aspects of the NIL is the anti-adhesive treatment of the applied mold because of the tendency of the resist polymer adhering to the mold during demolding process. In NIL process the stamp is repeatedly contacted the polymer film directly, so it should have high detachability and none contamination to insure the precision of the transfer and the lifetime of the mold.

Figure 2 illustrates the interaction between the template/resist and resist/substrate surfaces. When the template is detached from the cured resin, the cohesive force and adhesive force operate together between the interacting surfaces. The adhesion is based on the adsorption. There are two types of adsorption between the interfaces. One is the physisorption, also called physical adsorption. The imprint resist is mainly bonded through covalent forces in the

form of long-chain molecules. The fundamental interacting force of physisorption is caused by van-der-Waals force between two molecules. In the range of micro-/nano-size, the surface adhesion forces such as the van-der-Waals force and the electrostatic force are the dominant reasons of stiction between two adjacent surfaces. Two different materials can also form the compound at the join through chemical reaction. It is called chemisorption. In this case the adsorbate is bound by real chemical bond to the surface. Furthermore there is mechanical adhesion. The resist fill the cavity of the stamp in liquid form, and it holds surfaces together by cross-linkages after curing. The mechanical adhere force depends on the shape of the patterns (height, opening angle, diameter and so on).

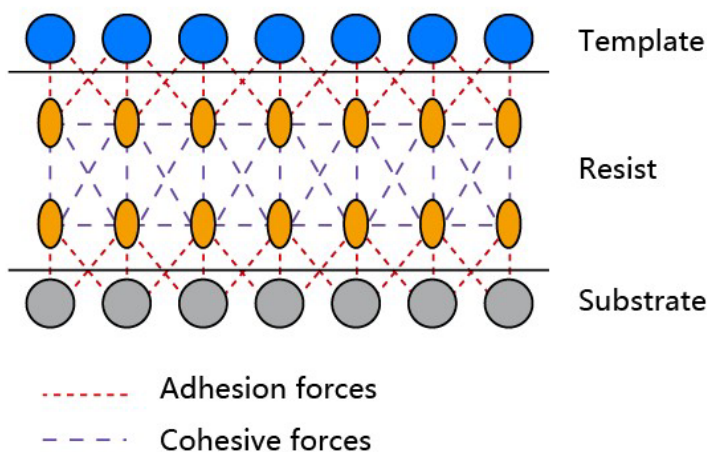


Figure 2. Schematic illustrations for mechanism of the adhesion in NIL.

#### 4. THE FABRICATION METHODS OF ANTI-ADHESIVE LAYER

Ideally, the adhesions between the interfaces should be asymmetry, which means the adhesion between the substrate/resist is expected higher than that between resist/template. There are two ways to reduce the adhesion between template and resist. One is to add release agent in the resist, the other method is to modify the mold surface with variety of release agents. In this chapter we will focus on the methods of modifying the mold. Since the first introduction of nanoimprint lithography, silicon, quartz, silicon dioxide and metal (nickel) have been the most reported materials for rigid mold.

## 4.1 Surface Characterization [15-17]

How to evaluate the quality of the anti-sticking layer is also an important issue. It covers widely from chemical to physical measurements. The modified surfaces are most commonly characterized by X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscope (AFM), Scanning Electron Microscope (SEM) and water contact angle measurement.

XPS, also known as electron spectroscopy for chemical analysis (ESCA), is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of the electrons that escape from the surface of the analyzed material deeping from 1 to 10 nm. The XPS technique can be utilized for sputter depth profiling to characterize thin films by quantifying matrix-level elements as a function of depth. It is highly surface specific due to the short range of the from the anti-adhesive layer excited photoelectrons.

Contact angle ( $\theta$ ) is a quantitative measure of the wetting of a solid by a liquid. It is determined by the resultant between adhesive and cohesive forces. A low value of contact angle indicates that the liquid spreads, or wets well, while a high contact angle indicates poor wetting. The contact angle provides an inverse measure of wetting. A higher contact angle means less surface energy, and demonstrates better anti-adhesion property.

Meanwhile, the surface morphology of the template influences mechanical adhesion. In virtue of AFM, the surface morphology, roughness, even adhesion, friction and wear characteristics can be confirmed.

On the surface of the mold, the thickness of the anti-adhesive film must be ultra thin. Otherwise they will affect the nanoscale feature and the critical dimension. The thickness can be measured by AFM, Spectroscopic Ellipsometer or SEM. In additional, the chemical and thermal stability of the film can be obtained by comparison the XPS spectra or the contact angle test after the modification or some imprintings.

## 4.2 Deposition of Anti-sticking Teflon-like Film [18-20]

When it comes to the concept of anti-adhesion, first of all, people would like think of polytetra- fluoroethylene (PTFE). PTFE gains its hydrophobic properties from the aggregate effect of carbon-fluorine bonds, as fluorocarbons demonstrate

mitigated London dispersion forces due to the high electronegativity of fluorine. PTFE has one of the lowest coefficients of friction against any solid. If a thin fluorinated film can be used as an anti-adhesion layer on the mold surface, the adhesion between surfaces can be reduced. Jaszewski et al have reported two ways to deposit ultra-thin Teflon-like films on nickel stamps, which are used in the surface structuring of thermoplasts in thermal nanoimprint lithography.

### ***1) Deposition of plasma polymerized PTFE films***

Plasma polymerization is an effective way to deposit the PTFE film. It is widely used as a new synthesis process in recent years. Plasma polymerization refers to formation of polymeric materials under the influence of plasma, and is also termed as “Glow Discharge Polymerization.” In the plasma polymerization process, a monomer gas is pumped into a vacuum chamber where it is polymerized by plasma to form a thin, clear coating. By selecting the monomer type and the energy density per monomer, the chemical composition and structure of the resulting thin film can be varied in a wide range. The plasma polymer films can be easily formed with thickness of 5000Å to 1μ. These plasma polymerized films are highly coherent and adherent to variety of substrates like conventional polymers, glass, metals. And they are highly dense and pinhole free. The PTFE polymer film deposition was carried out in a type of ‘self - thickness - limited’ mode, in which the thickness of the deposited polymer film is limited by the plasma parameters. Here the ultra-thin (<5 nm) teflon-like films have been deposited from a CF<sub>4</sub>/H<sub>2</sub> microwave discharge by using electron cyclotron resonance (ECR) condition. The deposition can be separated into two phases, a growth and a treatment phase. In the growth phase, a film with few CF<sub>2</sub> functionalities is deposited on flat nickel stamp. During the following treatment phase, etching and polymerization occur simultaneously during the fluorocarbon discharge. The dualism of etching and polymerization explains the thickness limiting behavior of the plasma. The final thickness and chemical composition of the polymer film are reached, when equilibrium is established between etching and polymerization. They are both dependent on the plasma parameters.

### ***2) Deposition of ion sputtered PTFE-like films***

Sputter deposition is a physical vapor deposition (PVD) method of depositing. Sputtering is a mechanism by which atoms are dislodged from the surface of a material as a result of collision with high-energy particles. Thus, PVD by Sputtering is a term used to refer to a physical vapor deposition (PVD) technique wherein atoms or molecules are ejected from a target material by high-energy particle bombardment so that the ejected atoms or molecules can condense

on a substrate as a thin film. Sputtering has become one of the most widely used techniques for depositing various metallic films onto a "substrate". It is also possible to sputter thin films of polymer using different gas mixture.

To form an anti-adhesive film, a Teflon material was used as the sputter target and  $\text{CHF}_3$  was selected as the sputtering gas. The  $\text{CHF}_3$  plasma was created in the deposition chamber by means of high radio frequency RF fields. The contained with free fluorinated ions plasma are accelerated by an electric field and randomly implanted on the nickel surface, thus slowly building up a film which has a grain structure. This film is chemically homogeneous due to the deposition characteristics. Compared with the polymerized film, the fluorocarbon chains in the internal network are short.

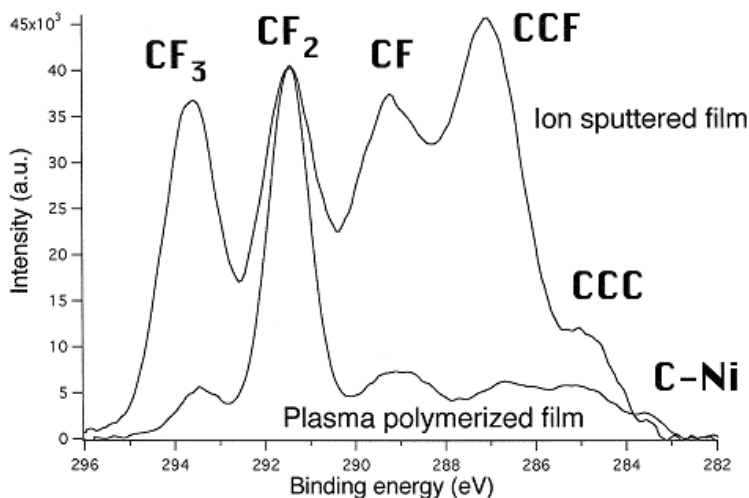


Figure 3. A comparison of the XPS spectra of two as-deposited PTFE-like films (bulk measurement).

After deposition, the nickel shim was characterized by XPS and their spectrum is shown in Figure 3. The XPS spectra indicate clearly that a thin film with  $\text{CF}_3$  ( $\approx 293.2$  eV),  $\text{CF}_2$  ( $\approx 291.4$  eV),  $\text{CF}$  ( $\approx 289.0$  eV),  $\text{CCF}$  ( $\approx 286.9$  eV),  $\text{CCC}$  ( $\approx 284.8$  eV) and  $\text{C-Ni}$  ( $\approx 283.6$  eV) was coated on the stamp surface by two different techniques. The  $\text{CF}$  bond in the film implies a low surface energy, and consequently excellent anti-adhesive properties. Generally the plasma deposited PTFE films yielded good anti-adhesive properties due to the high content of  $\text{CF}_2$  species. The higher  $\text{CF}$  content of the plasma polymerized film

indicates the presence of long linear chains, similar to that of pure PTFE. Ion Sputtering tends to form a more chemically heterogeneous film. Even with about equal amounts of the different CF species, the sputtered films are less PTFE like, while the CF<sub>2</sub> bonding is poorly formed and inhomogeneities in chemical bonding and clustering are observed. By monitoring the decrease of the C–Ni signal with the decreasing of electron take-off angle both thicknesses of the films was confirmed to about 5nm.

The good anti-sticking property of both films was demonstrated by the hot embossing with resist of Polycarbonate (PC) and Polymethylmethacrylate (PMMA). After 50 embossing no sticking of the resin occurred, and the thickness of the anti-adhesive layer remained constant. For both films, the percentage of CF<sub>2</sub> bonds decreased with the number of imprints, which is characterized by a transfer of fluorine from the film to the polymer.

It should be pointed out that the deposited thin Teflon-like films were generated on micrometer structured nickel stamps. The adsorbed polymer layer is not suitable for coating an imprint stamp with nanoscale features, while the polymeric structure makes it impossible, a monolayer to deposit. Meanwhile the polymer layer is adsorbed weakly on the stamp; the deposited antisticking layer must be renewed after some few imprints. Only by optimized imprint parameter (minimized embossing temperature and embossing time) hundreds of embossings are possible with one anti-adhesive PTFE like film.

### 4.3 Self Assembled Monolayer (SAM) as the Anti-adhesive Film [21-23]

In nanoimprint lithography a fluorinated self assembled monolayer (F-SAM) is one of the most mainly used anti adhesion layer. A self assembled monolayer (SAM) is an organized layer of amphiphilic molecules in which one end of the molecule, the “head group”, shows a special affinity for a substrate. In this case of application in NIL, the SAM of fluorinated silane release agent is created by the chemisorption onto a mold of silica or silicon from either the vapor or liquid phase deposition.

In the current study, the commercially available F<sub>13</sub>-OTCS (tridecafluoro-1,1,2,2- tetrahydrooctyl trichlorosilane) and octadecyltrimethoxysilane (OTMS) with fluorocarbon chains are the most widely reported fluorinated silane release agent to Si and SiO<sub>2</sub> surface modification. The mechanism of their formation is shown in Figure 4. In the modification process, the SAM was grafted on the fused silica stamp. Silanes with short chain lengths are deposited on the silica through

liquid or vapor phase. Before deposition, the mold is treated with piranha solution and rinsed with DI water to form large number of hydroxyl (-OH) groups attached on mold surface as shown in Fig. 4a. Then the silane head groups hydrolyze and form trisilanols (Fig. 4b). The  $\text{Si}(\text{OH})_3$  groups form covalent bonds with the hydroxyl groups on  $\text{SiO}_2$  surface, which is grafted to the silica surface (Fig. 4c). Subsequently condensation reaction goes on between neighbor molecules and the Si-O-Si covalent bonds can form (Fig. 4d). Finally, the networked coating is its ease of formation on the mold surface to lower the surface energy.

In the process the adsorbate fluorinated silane release agent molecules adsorb readily because they lower the surface energy of the substrate and are stable due to the strong chemisorption of the “head groups.” The monolayer created by covalently linking is very stable. The deposited film packs tightly due to van-der-Waals interactions, thereby reducing its own free energy and enhancing the anti-sticking property of the monolayer.

Liquid phase deposition methods are disadvantageous for the nanoscale feature due to insufficient wetting of the hydrophobic solvents on the hydrophilic stamp material. When the stamp features are in the nanometer size range, the vapor phase deposition is taking for prior consideration. Moreover, the monolayer by vapor phase deposition has a more uniform surface than that from liquid phase deposition.

In our research, an F-SAM of 1H, 1H, 2H, 2H -perfluorodecyltrichlorosilane ( $\text{F}_{17}$ -FDTS) is formed by vapor phase deposition to decrease the surface energy. The schematic of vapor phase deposition was outlined in Figure 5.

Before vapor deposition, the fused silica was first soaked in a piranha solution at 90 °C for 30 min and thoroughly rinsed with deionized (DI) water and dried with  $\text{N}_2$ . Since water reacts with chlorosilanes and polymerizes them, the modification was performed in a water free glove box environment. After the template was put in, the glove box was flushed with  $\text{N}_2$ . After the glove box being full with nitrogen atmosphere, the hotplate is then heated to 230 °C. Then some microliters  $\text{F}_{17}$ -FDTS are syringed on the Petri dish and both are covered immediately with a Petri dish. The coating is placed on in the airtight dish. When silanes with high vapor pressures come into contact with the template surface they react immediately to form a covalent linkage as described in Fig.4. After 3 h, the hotplate is cooled to room temperature and the excess FDTS is washed by anhydrous hexane to prevent FDTS polymerization.

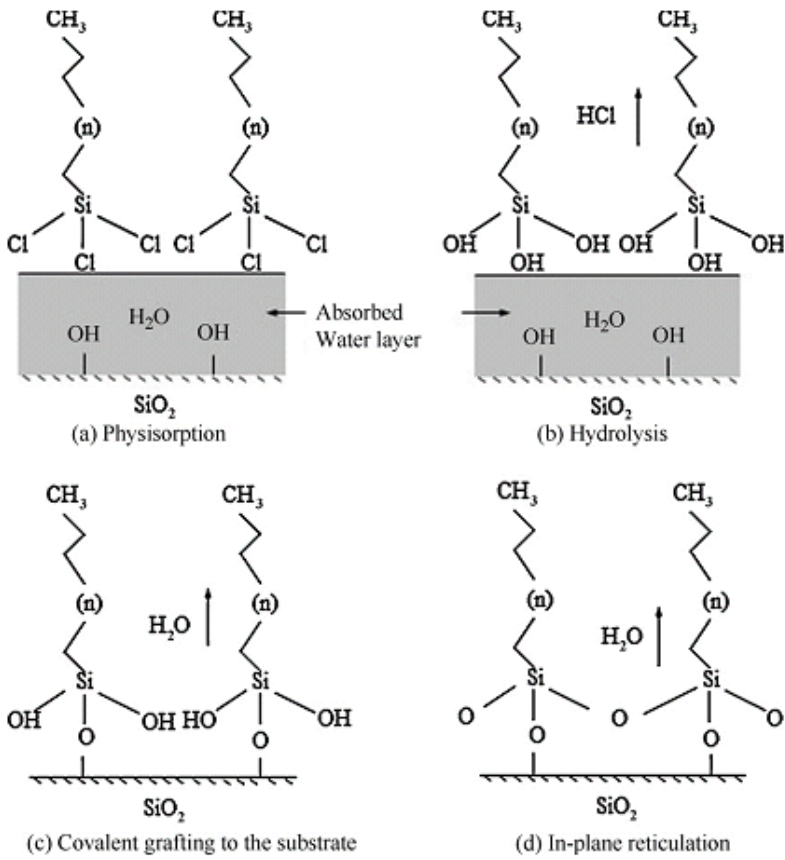


Figure 4. Scheme of the SAM formation mechanism on fused silica surface.

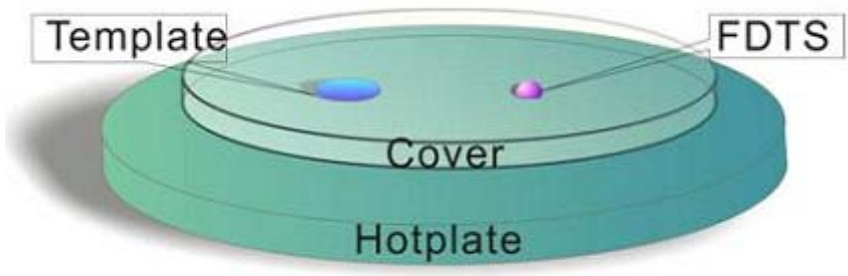


Figure 5 .Schematic of self-assembled monolayer on mold.

After modification, the contact angle is measured by using a contact angle goniometer SAM (OCA20, TBU 80E, Germany). Figure 6 shows photos of water droplet on the blank and SAM coated quarter mold, respectively. The water contact angle for blank stamp is  $33.01^\circ$ , but that for the FDTs coated stamp is up to  $113.11^\circ$ , indicating the high hydrophobic of SAM and the feasibility of its application in NIL. The water repellency of the stamp modified with FDTs is close to or better than that of F<sub>13</sub>-OTCS, which is tested to be  $112.97^\circ$ .

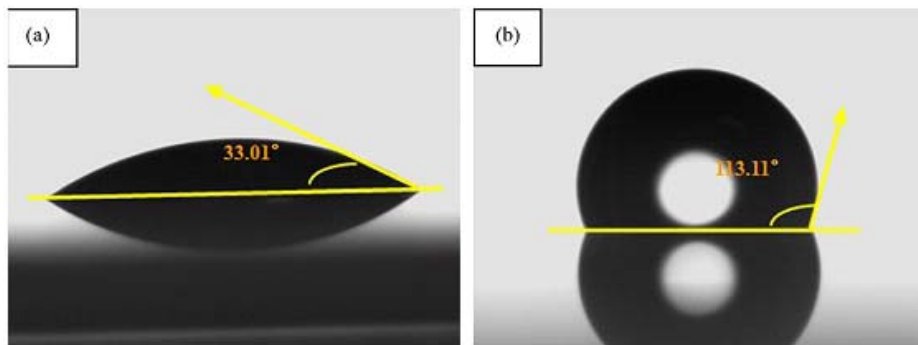


Figure 6. Photos of water droplet on (a) blank mold surface (b) SAM coated mold surface.

Then the quartz stamp was characterized by XPS and its spectra is shown in Figure 7. It can be seen that the F/C ratio of Mass is 3.8, the C (1s) spectra mainly consist of CF<sub>3</sub>, CF<sub>2</sub> and CF, which are centered at binding energies of 295eV, 292eV and 291eV, respectively. The C (1s) spectra indicated clearly that a thin organic layer successfully was coated on the surface of the quartz stamp. Besides, a broad peak could be seen from the spectra, which come from some organic impurities.

The UV-NIL was performed on an EVG620 (EVG Group, Austria). The commercially available AMONIL-MMS4 (AMO GmbH, Germany) is spun on the Si substrate with an initial thickness of 220nm. UV nanoimprinting using the templates with F-SAM coating in AMONIL resist demonstrates good pattern transfer fidelity and easy of emplate-resist separation. Figure 8 shows the SEM image of the imprinted resist. The structure with a feature sub 50nm can be seen in the resist. The margin of the imprinted pattern is rough. By repeating the imprinting over 100 times, the stamp still retained the ability of easy of demolding.

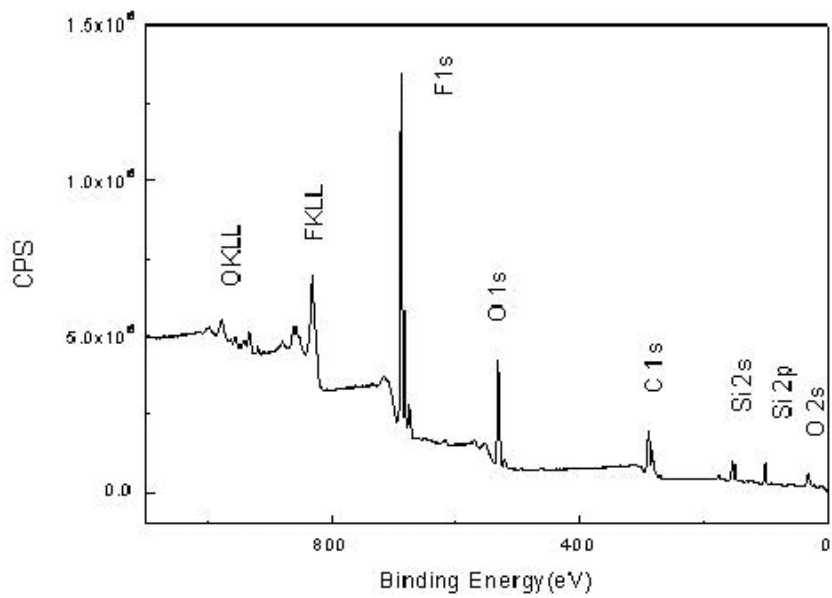


Figure 7. XPS survey spectra of the FDTS deposited quartz mold.

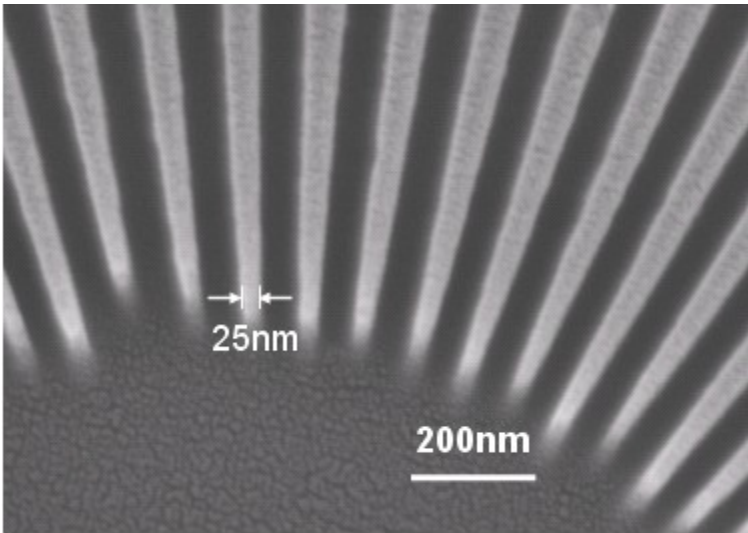


Figure 8. SEM micrographs of imprinted AMONIL patterns with sub 50nm line width.

#### 4.4 Fluorinated Diamond-Like Carbon (DLC) Thin Film [24-27]

As the name implies, diamond-like carbon (DLC) has some of the unique properties of diamond. It can be easily deposited on almost any material by plasma enhanced chemical vapor deposition (PECVD), including Si or quartz substrate. When applied in pure form it is as hard as natural diamond - or even harder, and these diamond coatings offer extraordinary protection against abrasive wear and attack from environment, which is particularly important for NIL because of the high mechanical forces applied during imprint. Besides the high hardness DLC has also low friction coefficient, and abrasion resistance and high UV transparent; it is meaningful for UV-NIL. Hence, in virtue of DLC coating the stamp can not only decrease surface energy and the friction between stamp and resist, but it can also maintain features precision of resists during the demolding.

However, the surface energy of the DLC is not low enough to meet the performance requirements as an anti-sticking layer of the nanoimprint mold. Thus, fluorinated DLC (F-DLC) has been applied as an enhanced anti-adhesive layer to a Si or quartz nanoimprint mold. Adding fluorine to a DLC film can reduce surface energy while maintaining a high hardness. The contact angle of the DLC and F-DLC surface was measured by contact angle meter. Figure 9 shows the measured contact angles of the both surfaces. The water contact angle of the DLC surface was measured 73°. Compared to pure DLC film the F-DLC surface presents lower surface energy, and the contact angle is 30° higher than that of the DLC surface. This result indicates the enhanced hydrophobic property of the F-DLC surface. K. Nakamatsu et al have reported that F-DLC was deposited by CVD as an anti-sticking layer for SiO<sub>2</sub> NIL templates with a thickness of 50 nm, and implemented for patterning of features with dimensions of a few hundreds of nanometers. The templates with F-DLC present a high chemical and physical stability during thermal nanoimprinting. After over 100 times imprinting the initial contact angle of the surface of the F-DLC-coated mold maintained 103°.

Besides anti-sticking layer DLC can be directly used as the mold material. M. Schwartzman et al have deposited 100-200nm DLC film on Si substrate in a plasma enhanced chemical vapor deposition system. With the help of E-Beam lithography and RIE the pattern was fabricated on the DLC. Then the stamp was exposed to fluorocarbon plasma to reduce the surface energy. The direct patterned DLC molds are very well suited for nanoimprint lithography. The imprint with sub-50 nm features has been obtained.

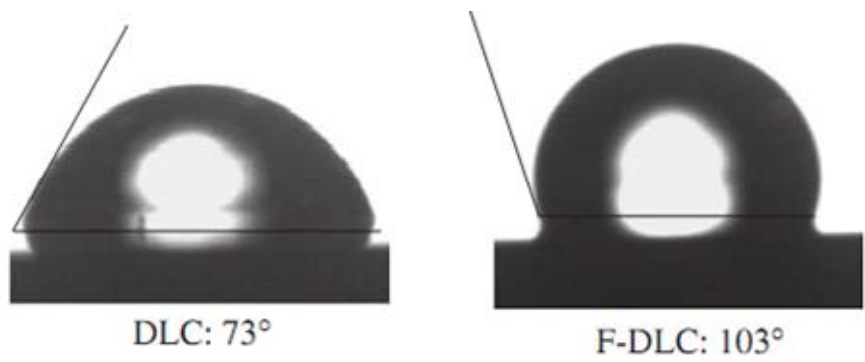


Figure 9. Photos of water droplet on (a) DLC surface (b) F-DLC coated surface.

4.5 Comparison of Anti-adhesive Material

We have already introduced three common release agents: PTFE like film, F-SAM and F-DLC. Table 1 is a comparison between them.

Table 1. Comparison of three materials as anti-adhesive layer

| Sample               | Contact angle | Thickness | Applicability      | Stability   |
|----------------------|---------------|-----------|--------------------|-------------|
| PTFE                 | --            | 5nm       | Thermal NIL        | degradation |
| F <sub>17</sub> -SAM | 113           | Monolayer | UV-NIL             | stable      |
| F-DLC                | 103           | 50nm      | Thermal and UV-NIL | stable      |

From the measurement of XPS the surfaces of the three layers were found to be overspread with hydrophobic CF<sub>x</sub> components. These CF<sub>x</sub> components decrease the surface energy of the mold obviously. Templates with them can easy be separated from the cured resin, and the imprint can keep high pattern transfer fidelity at nanoscale. Due to their UV transparent property F-SAM and F-DLC can be applied in UV nanoimprint. The fluorine mass of PTFE-like film exponentially decrease after an increasing number of embossings. Therefore, the parameter for the embossing must be very rigor, for example the embossing temperature and time must be minimized, or after some imprint a new protective film is re-deposited. The latter two are particularly suitable for reproduction. The contact angle of F-SAM is higher than that of the DLC, and the film thickness is thinner than that of DLC. But DLC film is the most stable one with high chemical

Copyright © 2011, Nova Science Publishers, Incorporated. All rights reserved.

stability and high wear resistance. It is not only a coating material but also can be patterned as mold.

## CONCLUSION

Nanoimprint has been developed rapidly in recent years. It is a very promising candidate to achieve optical lithography at 22nm node or below. As the adhesion between mold and resist plays a key role for the whole technology, the surface of the mold must be modified with an anti-sticking layer in order to avoid the adhesion between resist and template. In the chapter, we introduce the mechanisms of adhesion, methods of anti-adhesive treatment and their comparison. It is very important for the imprinted patterns without defects for the commercial application of NIL techniques.

## ACKNOWLEDGMENTS

This work is jointly supported by Municipal Natural Science Foundation 11ZR1432100), National 973 Program (2007CB935400) and Shanghai Postdoctoral Scientific Fund (11R21420900). The authors are grateful to all the other authors of related papers and some cited figures.

## REFERENCES

- Chou, SY; Krauss, PR; Renstrom, P. *J. Science*, 272 (5258), 85–7.
- Lebib, A; Chen. Yong, Cambri, E; Youinou, P; Studer, V; Natali, M. *Microelectronic Engineering*, 2002, 61-62, 371-377.
- Zankovych, S, Hoffmann, T, Seekamp J, Bruch, JU, Sotomayor Torres, CM. *Nanotechnology*, 2001, 12, 91-95.
- Gourgon, C, Lebib, A; Li, SP; Natali, M; Peyrade, D; Cambril, E. *Microelectronic Engineering*, 2001, 61-62, 385-392.
- Heidari, B; Maximov, I; Montellius, L. *Journal of Vacuum Science and Technology B*: 2000, 18, 3557-3560.
- Vratzon, B; Fuchs, A; Lemme, M; Henschel, W; Kurz, H. *Journal of Vacuum Science and Technology B*., 2003, 21, 2760-2764.

- Xia, QF; Keimel, C; Ge, HX; Zhao, ZN; Wu, W; Chou, SY. *Applied Physics Letters*, 2003, 83, 4417-4419.
- Carcenac, F; Vieu, C; Lebibi, A; Chen, Y; Manin, L. *Microelectronic Engineering*, 2000, 53, 163-166.
- Chou, SY; Krasuss, PR. *Microelectronic Engineering*, 1997, 35, 237-240. P. Gröning, A. Schneuwly et al., "Self-thickness-limited" plasma polymerization of an ultrathin antiadhesive film, *Vac. Sci. Technol. A* 14, 3043 (1996);
- Austin, MD; Chou, SY. *Applied Physics Letters*, 2002, 81, 4431-4433.
- The International Technology Roadmap for Semiconductors: 2009.
- S. Y. Chou, P. R. Krauss and P. J. Renstrom: *Appl. Phys. Lett.* 67(1995) 3 114.
- Kendall, K. "Adhesion: Molecules and Mechanics" *Science* 263, 1720 (1994).
- Habenicht, G. *Kleben*. Springer-Verlag, Berlin Heidelberg New York, 1997.
- Electron Spectroscopy for Atoms, Molecules and Condensed Matter, Nobel Lecture, December 8, 1981.
- Turner, DW.; Jobory, MI. Al (1962). "Determination of Ionization Potentials by Photoelectron Energy Measurement". *The Journal of Chemical Physics* 37: 3007.
- de Gennes, PG. (1985). "*Wetting: statics and dynamics*". *Reviews of Modern Physics* 57 (3): 827–863
- Jaszewski, RW. et al. Properties of thin anti-adhesive films used for the replication of microstructures in polymers. *Microelectronic Engineering* 35 (1997) 381-384
- Jaszewski, RW. et al. The deposition of anti-adhesive ultra-thin teflon-like films and their interaction with polymers during hot embossing, *Applied Surface Science* 143 1999 301–308
- Yasuda, H. "*Plasma Polymerization*" Academic Press Inc. 1985.
- Beck, M. Improving stamps for 10 nm level wafer scale nanoimprint lithography. *Microelectronic Engineering* 61 –62 (2002) 441 –448
- Zhou, WM; Zhang, J; BLiu, Y; Li, XL; Niu, XM; Song, ZT; Min, GQ; Wan, YZ; Shi, LY; Feng, SL. *Appl.Surf.Sci.*, 2008, 255, 2885.
- Truffier-Boutry, D. et al. *Microelectronic Engineering* 86 (2009) 669–672
- Ramachandran et al, Deposition and patterning of diamond like carbon, *J. Vac. Sci. Technol. B*, Vol. 24, No. 6, Nov/Dec 2006
- Nakamatsu, K. et al., Fluorinated Diamond-Like Carbon Coating as Antisticking Layer on Nanoimprint Mold, *Jpn. J. Appl. Phys.*, Vol. 45, No. 35 (2006).

- Schvartzman et al., Fluorinated diamondlike carbon templates for nanoimprint lithography, *J. Vac. Sci. Technol* Nov/Dec 2008.
- Tao L. et al, Durable diamond-like carbon templates for UV nanoimprint lithography, *Nanotechnology* 19 (2008) 105302.



## **Chapter 5**

# **ON THE DESIGN OF PRESS-FITTED AND ADHESIVELY BONDED JOINTS: STATIC AND FATIGUE TESTS IN STEEL AND ALUMINUM CONNECTIONS**

***D. Croccolo\*, M. De Agostinis and N. Vincenzi***

University of Bologna - DIEM, V.le Risorgimento 2, 40136 Bologna, Italy

## **ABSTRACT**

The work is focused on the static and fatigue strength of interference fitted connections supplemented with anaerobic adhesive (*Hybrid Joints*). Through axial release tests it is demonstrated that the addition of the adhesive always improves the performance of the joint: the main achievable benefits can be summarized in (i) the possibility of increasing the load transfer capability with the same joint geometry and (ii) reducing both the weight and the stress field of the joint with the same load transfer capability. The aim of the work is to provide some relevant information on the static and fatigue strength properties in case of both steel-aluminium components (*Mixed Hybrid Joints*) and steel-steel components (*Steel Hybrid Joints*). Proposed results derive from a collection of 200 experimental tests performed by the Authors on a high strength, single-component adhesive, which cures anaerobically (Loctite 648®).

---

\* Correspondence information: [dario.croccolo@unibo.it](mailto:dario.croccolo@unibo.it)

**Keywords:** anaerobic adhesive, interference joint design, bonding aluminium, hybrid joint.

**List of symbols:**

|                      |                                                                                 |
|----------------------|---------------------------------------------------------------------------------|
| $A$                  | coupling surface [mm <sup>2</sup> ]                                             |
| $D_{ext,H}$          | external hub diameter [mm]                                                      |
| $D_{int,H}$          | internal hub diameter [mm]                                                      |
| $D_C$                | coupling diameter [mm]                                                          |
| $D_{ext,S}$          | external shaft diameter [mm]                                                    |
| $D_{int,S}$          | internal shaft diameter [mm]                                                    |
| $E$                  | Young's modulus (shaft $E_S$ , hub $E_H$ ) [MPa]                                |
| $F_{int,ad}$         | interference, adhesive contribution to the axial release force of the joint [N] |
| $F_{coupling}$       | force to assembly shaft and hub in a press-fit [N]                              |
| $L_C$                | coupling length [mm]                                                            |
| $p_C$                | coupling pressure [MPa]                                                         |
| $Q_{S,H}$            | ratio between the internal and external shaft, hub diameters                    |
| $R_{z,a}$            | surface roughness [ $\mu$ m]                                                    |
| $U, Z$               | nominal, actual interference [mm]                                               |
| $\varepsilon_\theta$ | hoop strain                                                                     |
| $\mu_A$              | axial static coefficient of friction                                            |
| $\nu$                | Poisson's ratio (shaft $\nu_S$ , hub $\nu_H$ )                                  |
| $\tau_{ad}$          | adhesive static shear strength [MPa]                                            |

## 1. INTRODUCTION

Press-fitted and adhesively bonded joints (Hybrid Joints - *HJs*) are increasingly used as an alternative way to traditional structural joining techniques. The main benefits provided by the use of *HJ* can be summarized in the possibility of maximizing the load transfer (torque or axial) and reducing both the weight and

the stress field in the components, by taking advantage of the adhesive strength: the adhesive can either replace traditional joining techniques (i.e. keys, pins, interference-fits, bolted joints...) or can really improve the overall performances if used in combination with traditional techniques. As a matter of fact, dry press-fitted connections achieve only 20-30% of nominal surface contact (metal to metal), whereas the adhesive presence is able to fill the voids (air), reaching 100% of contact area [1]. However, the strength of *HJ* must be evaluated accurately, since it is affected by various factors, such as the coupling pressure [2], the type and the way of assembling [3,4], the type of materials in contact [5,6], the surface roughness [7], the curing type and the curing methodology [8], the operating temperature [9] and the loading type [10]. Most of the technical literature about *HJs* is mainly focused on steel-steel components (Steel Hybrid Joints – *SHJs*) [2-5,11,12] and on their verification technique (non-destructive testing) [13,14]. The use of different materials implies the diffusion of new joining technologies. For example, the automotive industry is strongly developing lightweight and energy efficient vehicles [15-17]: efforts are mainly directed towards the substitution of steel by aluminium or other lightweight materials. Therefore, this work aims at providing some relevant information on static and fatigue strength properties in presence of aluminium components (Mixed Hybrid Joints - *MHJs*) and to perform a comparison with steel ones (*SHJs*): all the analysed connections are press-fitted and bonded via a high strength, single-component adhesive that cures in absence of oxygen (Loctite 648® [18]). *AMHJ* can be realized by an aluminium shaft coupled with a steel hub (aluminium-steel), or by a steel shaft coupled with an aluminium hub (steel-aluminium). The external forces (coupling, release or fatigue loads) are always applied to the shaft.

## 2. METHODOLOGY

Tested specimens are shaft hub cylindrical joints made of different materials. Both shafts and hubs were realized in steel (39NiCrMo3 [19]) and in aluminium (6082T6 [20]): the chosen alloys are widely used in the automotive industry. An example of the components is reported in Fig. 1, while material properties, obtained by direct testing according to UNI-EN 10002, are reported in Table 1. A total of 200 specimens were tested with different geometrical dimensions: the range of their variations is reported in Table 2.

A fundamental design parameter of press-fitted couplings is the axial release force  $F_{int}$  [N], reported in Eq. (1), which depends on the axial static friction coefficient  $\mu_A$ , coupling pressure  $p_C$  [MPa] and contact surface  $A$  [mm<sup>2</sup>].

**Table 1. Material properties of the specimens used (evaluation according to UNI EN 10002)**

|                            | <i>E [GPa]<br/>Young's<br/>modulus</i> | <i>ν<br/>Poisson's<br/>ratio</i> | <i>S<sub>y</sub><br/>[MPa]<br/>Yield<br/>stress</i> | <i>S<sub>U</sub> [MPa]<br/>Ultimate<br/>stress</i> |
|----------------------------|----------------------------------------|----------------------------------|-----------------------------------------------------|----------------------------------------------------|
| <i>Steel (39NiCrMo3)</i>   | 207                                    | 0.29                             | 900                                                 | 1,050                                              |
| <i>Aluminium (6082 T6)</i> | 69                                     | 0.33                             | 304                                                 | 343                                                |

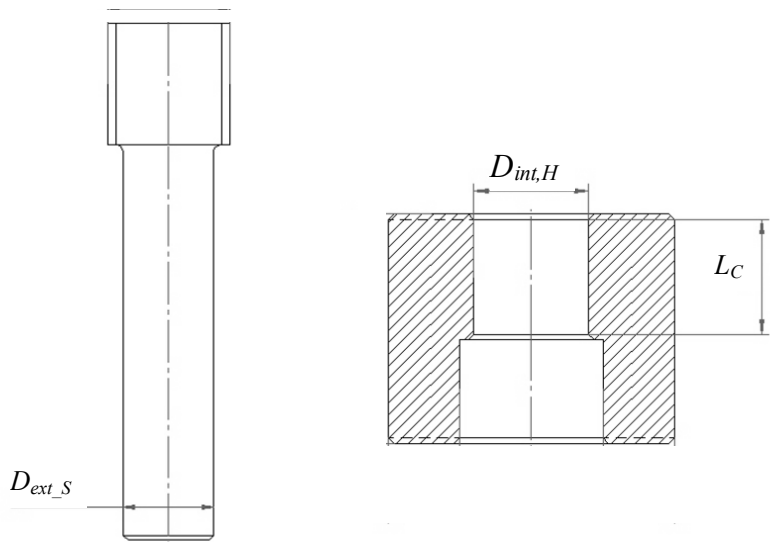


Figure 1. Example of tested specimen: shaft (left) and hub (right).

**Table 2. Range of variation of geometrical parameters in tested interference joints**

| <i>D<sub>int,S</sub><br/>[mm]</i> | <i>D<sub>C</sub><br/>[mm]</i> | <i>D<sub>ext,S</sub><br/>[mm]</i> | <i>L<sub>C</sub><br/>[mm]</i> | <i>U<br/>[mm]</i> | <i>p<sub>C</sub><br/>[MPa]</i> |
|-----------------------------------|-------------------------------|-----------------------------------|-------------------------------|-------------------|--------------------------------|
| 0 ... 10                          | 20 ... 30                     | 40 ... 50                         | 20 ... 35                     | 0.01 ... 0.06     | 20 ... 80                      |

$$F_{\text{int}} = \mu_A \cdot p_C \cdot A \quad (1)$$

The axial static friction coefficient  $\mu_A$  strictly depends on the coupled materials and the surface conditions of the components:  $\mu_A$  is usually within the range 0.04-0.7 [21]. Thus, it must be accurately evaluated in order to reduce the variation in the  $F_{\text{int}}$  calculation. The coupling pressure  $p_C$ , which is generated by the actual interference  $Z$  [mm] between the shaft and the hub, is a function of the stiffness of the coupled components, as highlighted in Eq. (2) [22,23].

$$p_C = \frac{Z/D_C}{\frac{1}{E_H} \cdot \left( \frac{1+Q_H^2}{1-Q_H^2} + \nu_H \right) + \frac{1}{E_S} \cdot \left( \frac{1+Q_S^2}{1-Q_S^2} - \nu_S \right)} \quad (2)$$

$D_C$  [mm] is the coupling diameter, equal to the mean of the external shaft  $D_{\text{ext},S}$  [mm] and the internal hub  $D_{\text{int},H}$  [mm] diameters,  $E$  [MPa] and  $\nu$  are the Young's modulus and the Poisson's ratio, respectively (hub:  $E_H$ ,  $\nu_H$ ; shaft:  $E_S$ ,  $\nu_S$ ) and  $Q$  is the ratio between the internal and external diameters of the hub ( $Q_H = D_{\text{int},H}/D_{\text{ext},H}$ ) and of the shaft ( $Q_S = D_{\text{int},S}/D_{\text{ext},S}$ ). The actual interference  $Z$  [mm] is lower than the nominal one  $U$  [mm] when the assembly is realised by means of a hydraulic press with the shaft press-fitted into the hub and both set at the same temperature. If the stiffness of the parts has a similar value (for example, in case of the same material type), the difference between  $U$  and  $Z$  can be related to the surface roughness  $R_a$  or  $R_z$  [mm] of the components (hub:  $R_{a-z,H}$ ; shaft:  $R_{a-z,S}$ ), as proposed in [24,25] and reported in Eq. (3).

$$Z = \begin{cases} (D_{\text{ext},S} - D_{\text{int},H}) - 0.8 \cdot (R_{z,H} + R_{z,S}) \\ (D_{\text{ext},S} - D_{\text{int},H}) - 3 \cdot (R_{a,H} + R_{a,S}) \end{cases} \quad (3)$$

The relationships reported in Eq. (3) were obtained empirically from several tests performed on steel-steel assemblies. In order to evaluate the actual coupling pressure accurately, especially in presence of different coupled materials, it is advisable to apply, on the external surface of the hub, a strain gauge, which is able to provide the external hoop strain  $\varepsilon_\theta$ , as reported in Figure 2. In light of this,  $\varepsilon_\theta$  can be simply related to  $p_C$  by applying the thick walled cylindrical theory

reported in Eq. (4), and well demonstrated by Croccolo et al. [26]. Finally, the contact surface  $A$  is a function of the coupling diameter  $D_C$  and of the coupling length  $L_C$  [mm]:  $A = \pi \cdot D_C \cdot L_C$ .

$$p_C = \frac{E_H \cdot \varepsilon_\theta \cdot (1 - Q_H^2)}{2 \cdot Q_H^2} \quad (4)$$



Figure 2. Examples of strain gauge application on the external surface of the hub (quarter-bridge connection in Wheatstone circuit).

The production of *HJs* begins with the spreading of the anaerobic adhesive on the female component (the hub), followed by the assembly operation performed with the same procedure used for press-fitted couplings. Anaerobic adhesives belong to the large family of thermosetting acrylic polymers: kept stable as a one-part liquid by the oxygen of the air, they harden easily between 15°C and 50°C if entrapped in airless environments and exposed to active metals (e.g. steel, aluminium, titanium, copper,...). Both prerequisites are naturally met in the small roughness gap between conformal metal surfaces, which abound in all sort of mechanical components. This makes of anaerobics an ideal joining method in the field of machine design. The mechanical interference and the adhesive strength act as parallel connected springs [12] and, therefore, the axial release force of *HJs* can be evaluated by applying the superposition of these effects, as shown in Eq. (5): the two contributions (interference and adhesive) can be calculated separately as described in the next sections.

$$F_{tot} = F_{int} + F_{ad} = (\mu_A \cdot p_C + \tau_{ad}) \cdot A \quad (5)$$

The friction coefficient  $\mu_A$  is considered constant, both in presence and in absence of adhesive, because metals remain in contact (without any adhesive interposition) in the peaks of the roughness whereas the liquid adhesive fills the voids of all depressions [3]. The adhesive contribution  $F_{ad}$  [N] depends on the coupling surface  $A$  and the mean adhesive static strength  $\tau_{ad}$  [MPa], which must be experimentally calculated.

### 3. EXPERIMENTAL RESULTS

*SHJs* and *MHJs* were studied separately. In case of *SHJs* the same specimens were used and reused for several static and dynamic tests because the coupling and decoupling operations do not spoil them [1-3, 12-14]. The geometrical dimensions (internal diameter of the hub and external diameter of the shaft) do not change throughout the tests and therefore the interference level and the coupling pressure, in the same specimen, are constant. Conversely, in case of *MHJs*, several aluminium shafts and hubs were realized. In fact, because of the different hardness of the materials, the coupling and decoupling operations cause the spoiling of the aluminium, that change the nominal dimensions, so that their reuse is impossible. This occurrence is well highlighted by the residual dusts visible on the coupled surfaces, and by the scratches on the cleaned components (see aluminium shaft reported in Figure 3).

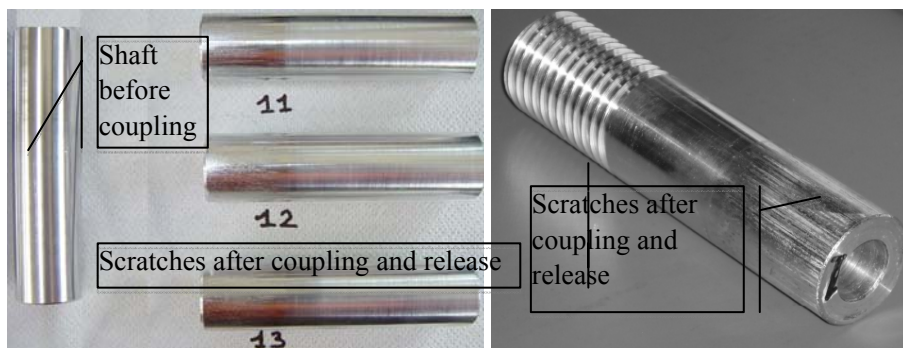


Figure 3. Example of scratches in aluminium shafts after one coupling and release operation.

### 3.1 Static Strength

Three sets of tests were performed statically in order to evaluate  $HJ$  performances in comparison to purely press-fitted ones: (i) dry press-fitted, (ii) adhesively bonded slip-fitted and (iii) adhesively bonded press-fitted.

#### 3.1.1 Dry press-fitted Joints

Eight specimens were coupled and decoupled in order to evaluate the axial static friction coefficient  $\mu_A$ , both for steel-steel and steel-aluminium joints: the mean value of  $\mu_A$  was equal to 0.21 (standard deviation 0.02) for steel-steel connections and equal to 0.46 (standard deviation 0.03) for steel-aluminium connections. Tests were performed on a 250 kN hydraulic press. The actual coupling pressure  $p_C$  was evaluated according to Eq. (4). Finally, the axial static friction coefficient  $\mu_A$  was calculated by applying Eq. (6), in which  $F_{int}$  is given by the load cell of the press at the initial release (movement) of the specimens. An example of experimental data for steel-aluminium connections is reported in Table 3.

$$\mu_A = \frac{F_{int}}{p_C \cdot A} \quad (6)$$

The actual interference  $Z$  is well forecasted by applying Eq. (3) only for steel-steel connections; in presence of aluminium,  $Z$  depends only on its surface roughness variation before ( $R_{a,H \text{ before}}$ ) and after ( $R_{a,H \text{ after}}$ ) the coupling (Table 3). This occurrence is well shown in the example of Figure 4 between a steel shaft and aluminium hub, before and after the coupling. It is possible to identify some regions where aluminium dust has been transferred from the hub to the shaft. This is mainly related to the different stiffness of coupled materials (aluminium and steel), which produces a high wear of the softer material (aluminium) during the press-fit operation [28]. As a matter of fact, in presence of aluminium (Table 3), the axial force needed to join the parts ( $F_{coupling}$ ) is always higher than the release one ( $F_{int}$ ).

In presence of aluminium shaft and steel hub (aluminium-steel) several problems related to the low stiffness of aluminium occur to the connection. As a matter of fact, due to the high elastic deformation of aluminium, the actual interference widely changes when the shaft is loaded both in tension and in

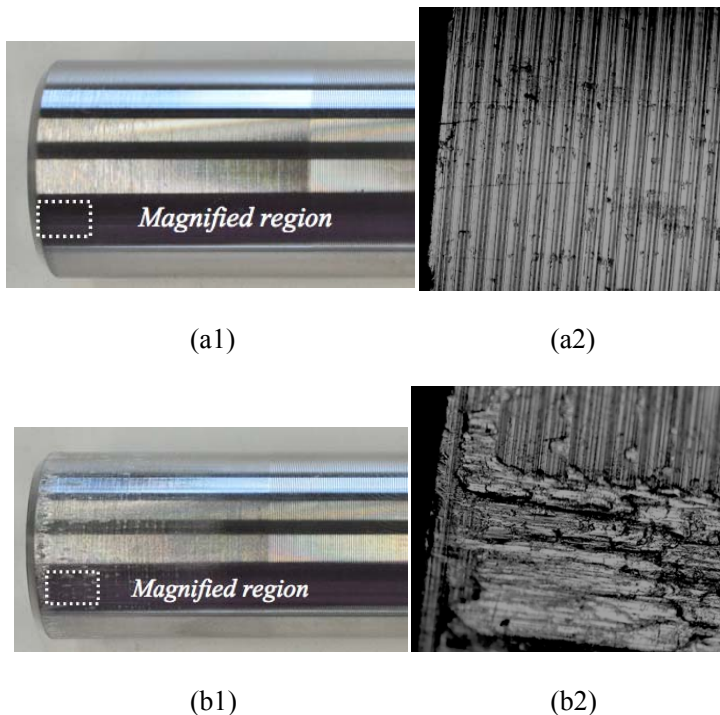


Figure 4. Pictures of steel shaft surfaces before coupling (a) and after release (b) operations: (1) 1x magnification, (2) 50x magnification.

**Table 3. Summary of results for steel-aluminium joints purely press-fitted**

| <i>Dry press-fitted joints</i> | $U$ [mm] | $p_c$ [MPa] | $R_{a,H}$ before [μm] | $R_{a,Shefore}$ [μm] | $R_{a,Hafter}$ [μm] | $R_{a,S}$ after [μm] | $F_{coupling}$ [kN] | $F_{int}$ [kN] | $\mu_A$ |
|--------------------------------|----------|-------------|-----------------------|----------------------|---------------------|----------------------|---------------------|----------------|---------|
| 1                              | 0.026    | 40.0        | 2.44                  | 0.99                 | 0.30                | 1.03                 | 26.50               | 26.00          | 0.52    |
| 2                              | 0.016    | 26.1        | 2.44                  | 0.92                 | 0.34                | 1.05                 | 16.50               | 14.00          | 0.43    |
| 3                              | 0.016    | 27.2        | 2.44                  | 0.89                 | 0.69                | 0.90                 | 17.90               | 15.00          | 0.44    |
| 4                              | 0.019    | 35.5        | 2.44                  | 1.00                 | 0.51                | 1.15                 | 23.00               | 21.00          | 0.47    |
| 5                              | 0.016    | 25.3        | 2.45                  | 0.97                 | 0.40                | 1.10                 | 15.50               | 13.00          | 0.41    |
| 6                              | 0.018    | 32.1        | 2.44                  | 0.91                 | 0.37                | 1.01                 | 22.00               | 19.50          | 0.48    |
| 7                              | 0.021    | 33.9        | 2.44                  | 0.95                 | 0.32                | 0.97                 | 22.60               | 20.00          | 0.47    |
| 8                              | 0.024    | 38.1        | 2.45                  | 0.94                 | 0.34                | 1.02                 | 26.60               | 23.50          | 0.49    |
|                                |          |             |                       |                      |                     |                      |                     |                |         |
| <b>Mean value</b>              | 0.020    | 32.3        | 2.44                  | 0.95                 | 0.41                | 1.03                 | 21.30               | 19.00          | 0.46    |

compression [26]. In tension, the actual interference decreases (Poisson's effect), so that the joint performances decrease dramatically; whereas in compression the actual interference increases, resulting in an overestimation of the joint strength (Figure 5). This occurrence is well highlighted by the comparison between aluminium and steel shafts in the force trend during the coupling and release (decoupling) phase: non-linear force trend for aluminium (Figure 6a) points out the variation in interference due to the load variation. Mixed joints with steel shaft and aluminium hub (steel-aluminium) are, on the contrary, able to overcome the aforementioned issues and, therefore, they are the most suitable to be used [26].

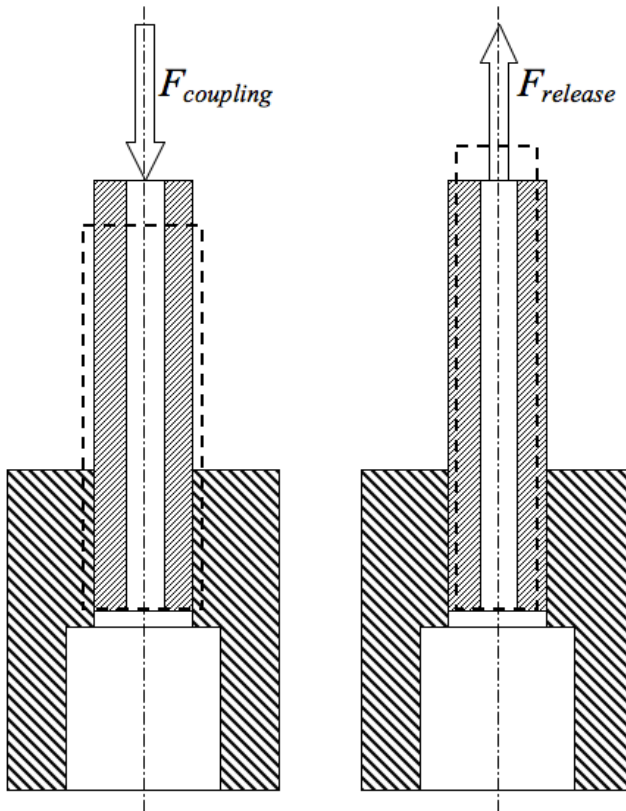


Figure 5. Variation in interference of the aluminium shaft during the coupling and release phase.

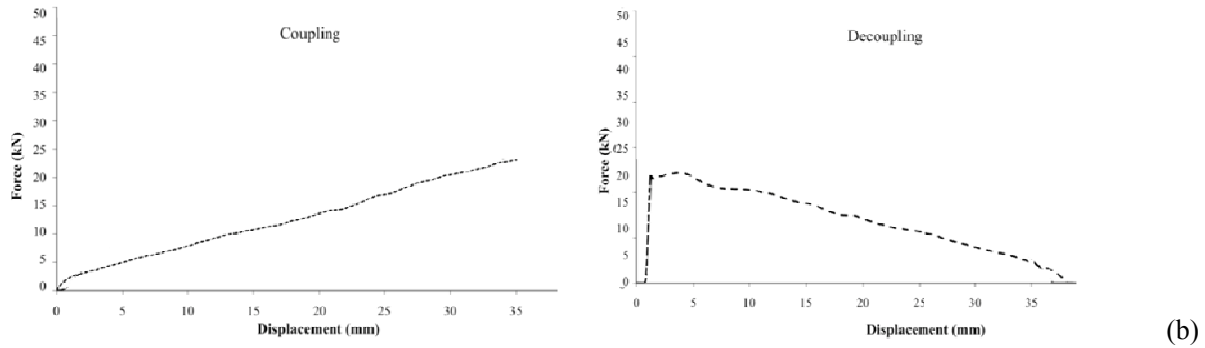
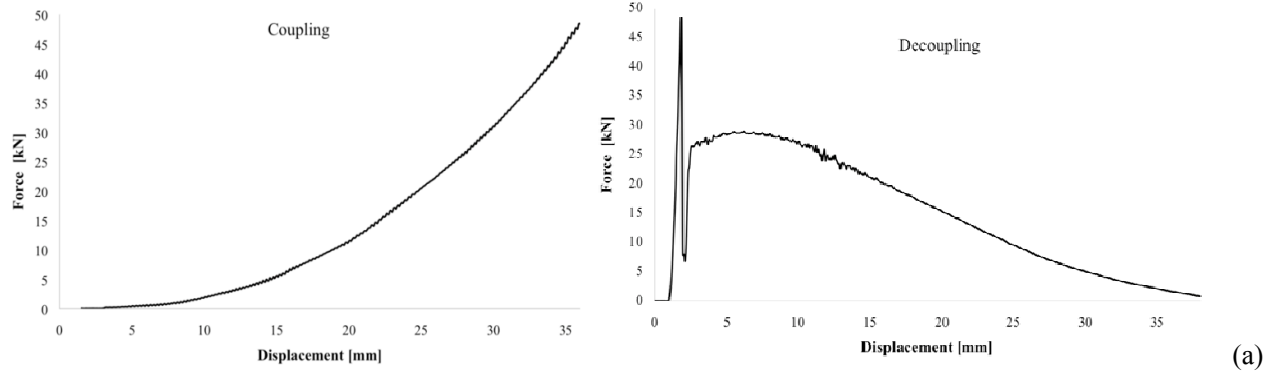


Figure 6. Example of force trend during the coupling and release (decoupling) process: (a) aluminium shaft and (b) steel shaft.

3.1.2 Adhesively Bonded Slip-fitted Joints

A second set of 8 tests was performed on slip-fitted couplings, which had a clearance between the shaft and the hub. These tests allow evaluating the mean strength of the pure anaerobic adhesive ( $\tau_{ad}$ ), without the interference contribution. The clearance value (difference between diameters) was realised inthe range 0.02-0.05 mm since this value is associated with the maximum strength for *SHJ*, as showed by Sekercioglu et al. [4]. Specimens were cleaned with Loctite 7061®, which is a general purpose cleaner for preparing surfaces to be bonded with adhesive, then, specimens were cured for 24 h at 40°C. While steel-steel specimens showed a cohesive failure, steel aluminium specimens showed an adhesion failure, in which the adhesive always remained on the steel adherend. This occurrence is mainly due to the lower value of surface energy of aluminium (*wettability*) with respect to steel, as well demonstrated by Borsellino et al. [29] and Comyn [30] by the determination of the contact angles at solid/liquid interfaces. The mean shear strength  $\tau_{ad}$  of the adhesive for slip-fittedsteel-steel joints is equal to 24.5 MPa (standard deviation equal to 0.5 MPa) while for steel-aluminium joints equal to 9.6 MPa (standard deviation equal to 0.2 MPa). Results can be compared in Figure7 [4, 32].



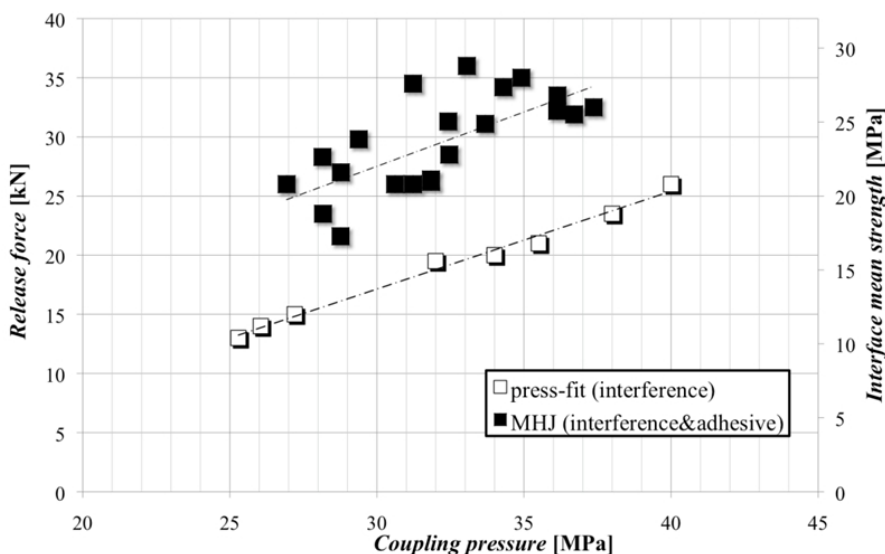
Figure 7. Mean adhesive shear strength in case of slip-fitted joints.

### 3.1.3 Adhesively Bonded Press-fitted Joints

Finally, a third set of 20 different tests (both for *SHJs* and *MHJs*) was performed on press-fitted and adhesively bonded connections, with the purpose of evaluating the total strength of *HJs*, compared to the previous ones. An example of results for steel-aluminium joints plotted in Figure 8 highlights the increase in scatter for *HJs* with respect to the two previous sets of tests. The static strength of the adhesive  $F_{ad}$  and the adhesive mean shear strength  $\tau_{ad}$  were derived from Eq. (7), in which the interference contribution ( $F_{int}$ ) is given by applying Eq. (1), while the total axial release force ( $F_{tot}$ ) is given by the load cell of the hydraulic press.

$$F_{ad} = F_{tot} - F_{int} \Rightarrow \tau_{ad} = \frac{F_{tot} - F_{int}}{A} = \frac{F_{tot}}{A} - \mu_A \cdot p_C \quad (7)$$

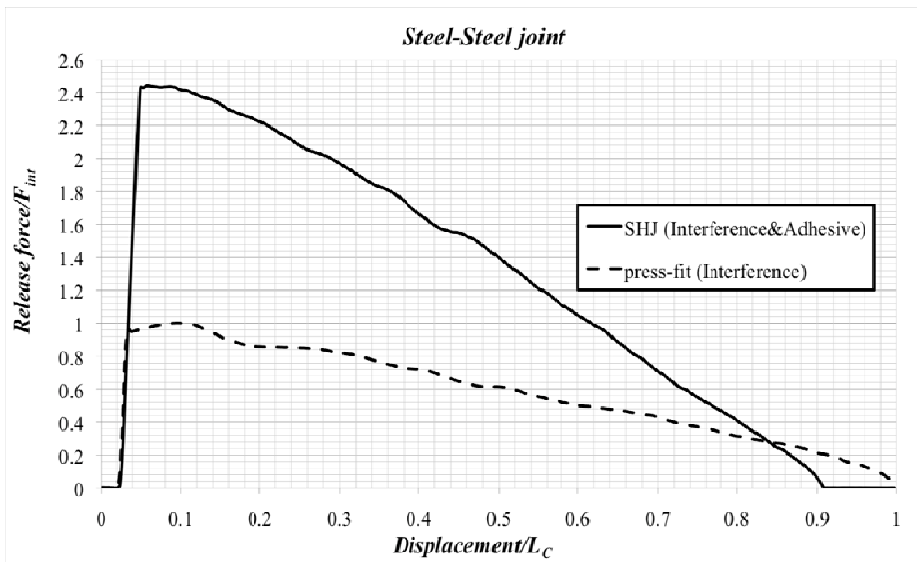
Since the coupling is realized by a press-fit, the growth of release force (Figure 8) can be attributed to the amount of adhesive that actually remains at the interface of coupled surfaces. Accordingly, the frictional contribution was considered constant.



Comparison between purely (dry) press-fitted and *MHJ*: axial release force and interface mean strength as a function of the coupling pressure.

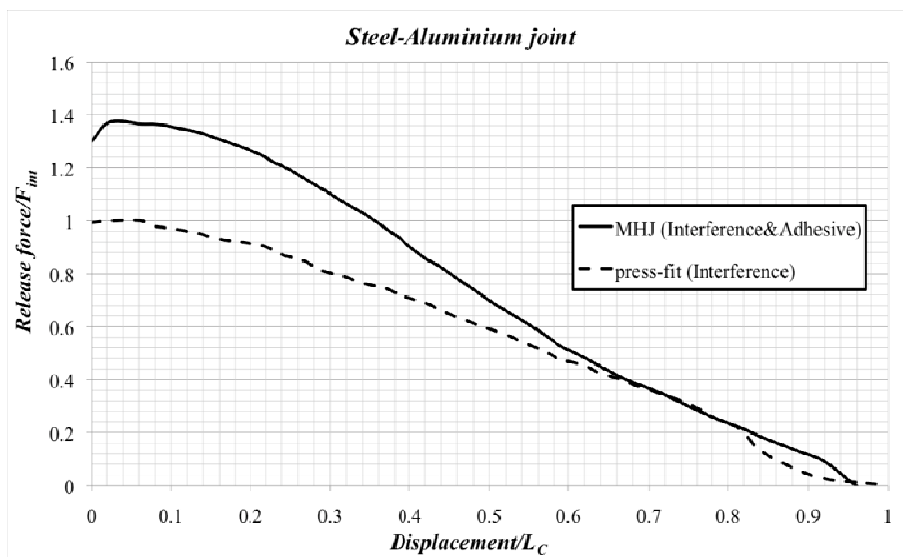
The overall performance of the joint increases both in case of *SHJs*, as demonstrated in [1-8,12-14,26], and in case of *MHJs*[32]. The axial release force and the interface mean strength are plotted in Figure8 as a function of the actual coupling pressure. In the case of purely (dry) press-fitted joints, the interface mean strength is equal to  $\mu_A p_C$  whereas in case of *HJ* it is equal to  $\mu_A p_C + \tau_{ad}$ . The adhesive mean strength  $\tau_{ad}$  is within the range of 6-12MPa for *MHJs* (average value equal to 9.2MPa, standard deviation 1.9MPa) and within the range of 16-23 MPa for *SHJs* (average value equal to 18.9 MPa, standard deviation 3.4 MPa). The average value of  $\tau_{ad}$  in press-fitted and adhesively bonded joints is close to that found for slip-fitted joints, even if the standard deviation increases.

An example of the force trend plotted as a function of the displacement during the release phase is reported in Figure9. Values, for both *SHJ* [26] (Figure9a) and for *MHJ*[32] (Figure9b), have been conveniently made dimensionless by normalizing them to the interference release force ( $F_{int}$ ) and to the coupling length ( $L_c$ ) in order to compare different geometries (see Table 2).



(a)

Figure 9. (Continued).



(b)

Figure 9. Release forces for HJs compared to the purely press-fitted ones: (a) SHJ [26] and (b) MHJ [32].

In presence of steel shaft, the total and the adhesive strengths have been noticed to be strictly related to the maximum assembly (coupling) force, as reported for example in Figure 10 and in Figure 11 for *MHJs*. In light of this, it is possible to define two constants,  $K_1$  and  $K_2$ , calculated by the ratio between the total strength and the coupling load, and by the ratio between the adhesive strength and the coupling load, respectively (Eq. 8). Their trends are reported in Figure 12, as a function of the coupling pressure.

$$\begin{cases} K_1 = \frac{F_{tot}}{F_{coupling}} = \frac{F_{int} + F_{ad}}{F_{coupling}} \\ K_2 = \frac{F_{ad}}{F_{coupling}} \end{cases} \quad (8)$$

For steel-aluminium connections (*MHJs*)  $K_1 \approx 1.23$  and  $K_2 \approx 0.47$ , while for steel-steel connections (*SHJs*)  $K_1 \approx 1.12$  and  $K_2 \approx 0.56$ .

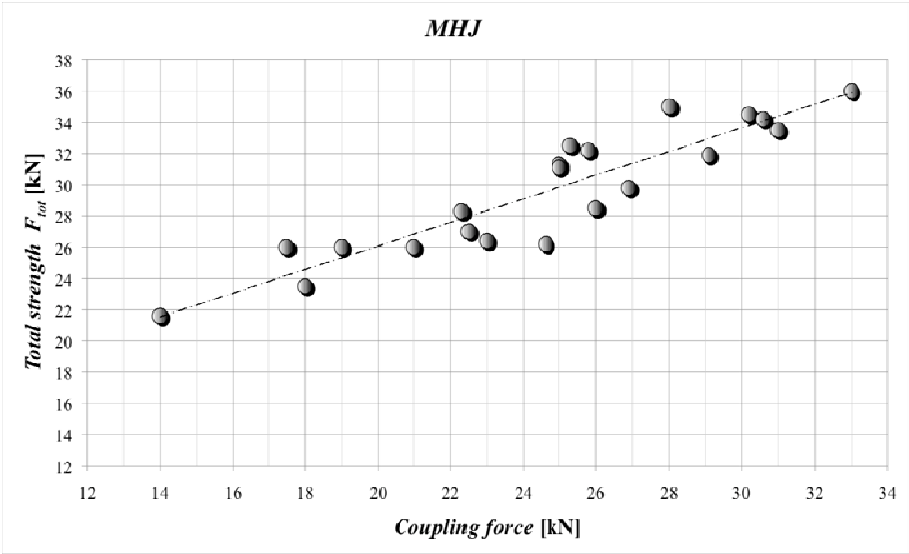


Figure 10. Total strength  $F_{tot} = F_{int} + F_{ad}$  plotted as a function of the coupling force.

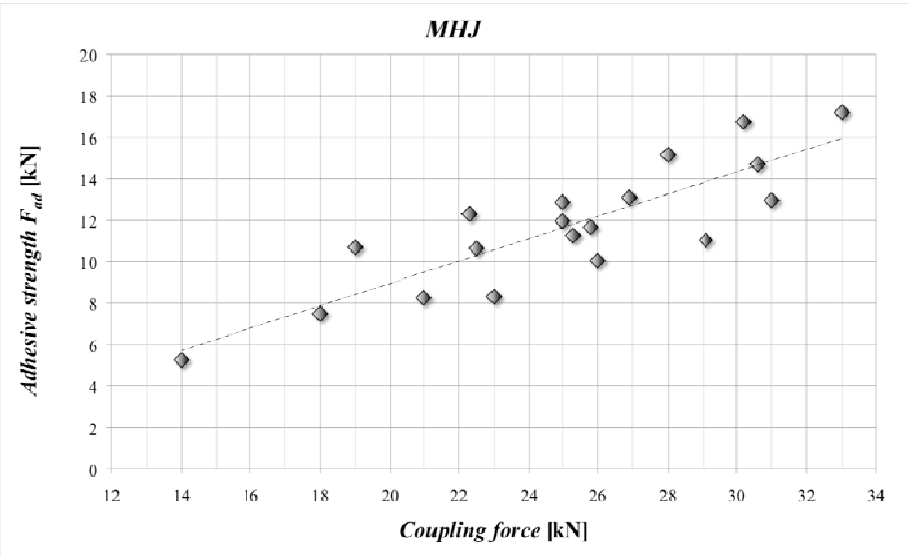


Figure 11. Adhesive strength contribution  $F_{ad}$  plotted as a function of the coupling force.

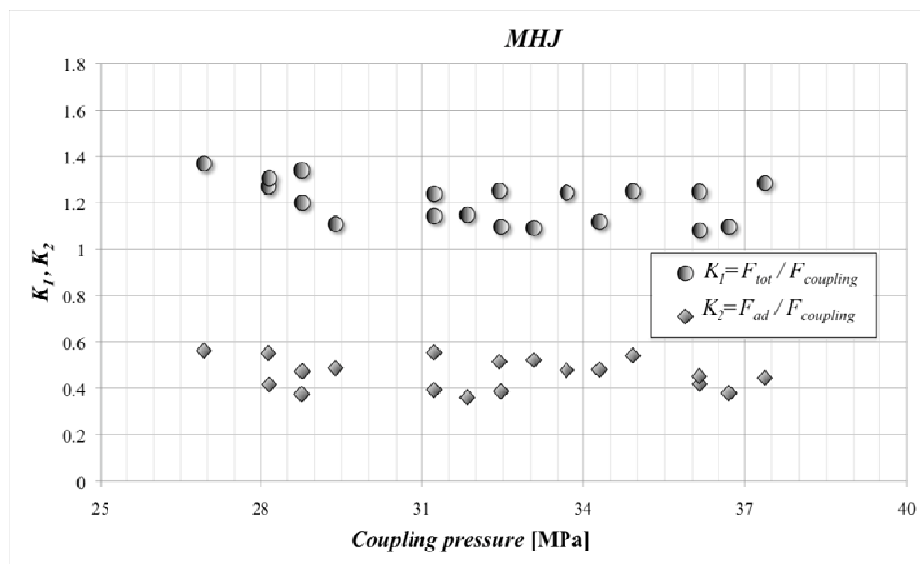


Figure 12.  $K_1$  and  $K_2$  trends as a function of the coupling pressure.

### 3.2 Fatigue Strength

A total of 15 fatigue tests based on stress-life ( $S-N$ ) approach were performed on slip-fitted joints, with the purpose of evaluating the purely anaerobic adhesive fatigue strength [31,32] both in  $SHJs$  and in  $MHJs$ . The stress ratio  $R$  was set equal to 0.1 (nearly “pulsating tension” condition) while the test frequency  $f$  was set equal to 20 Hz. An example, for  $MHJs$ , of the shear stress range  $\Delta\tau$  [MPa], dimensionless with respect to the static shear stress is reported in Figure13, as a function of the number of cycles  $N$ , while the comparison between  $MHJs$  and  $SHJs$  is reported in Figure14.

The ratio between the shear stress range and the static shear strength at  $10^6$  cycles results equal to 0.62 ( $\Delta\tau_{\infty} \approx 0.62 \cdot \tau_{ad\_MHJs}$ ) for  $MHJs$  and to 0.35 ( $\Delta\tau_{\infty} \approx 0.35 \cdot \tau_{ad\_SHJs}$ ) for  $SHJs$  (remember that the static shear strength  $\tau_{ad}$  for  $SHJs$  is different than for  $MHJs$ !).

At last, fatigue results determined for slip-fitted steel-aluminium joints were applied to 6 different press-fitted steel-aluminium ones (with coupling pressures in the same range as of the ones tested statically), in order to verify the  $S-N$  curve

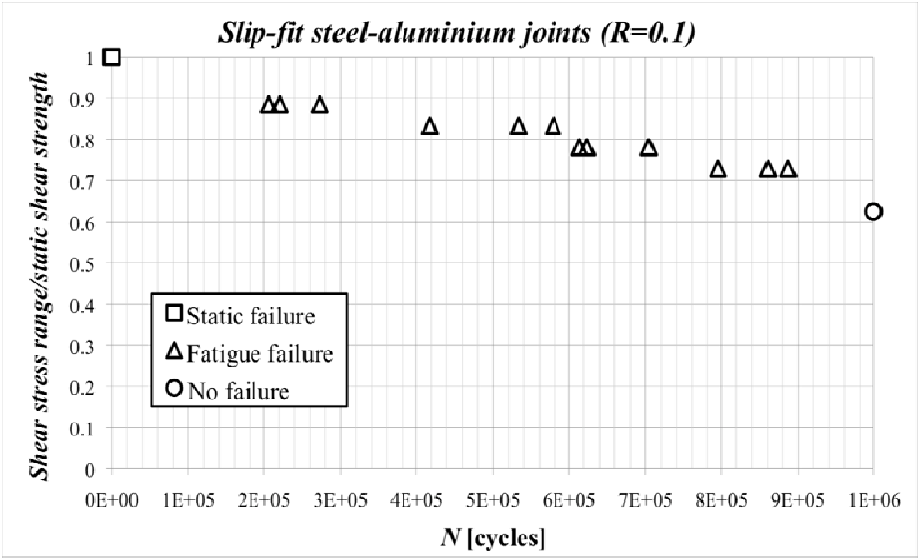


Figure 13.  $\Delta\tau/\tau_{ad}$ - $N$ curve for slip-fitted steel-aluminium joints (stress ratio  $R=0.1$ ).

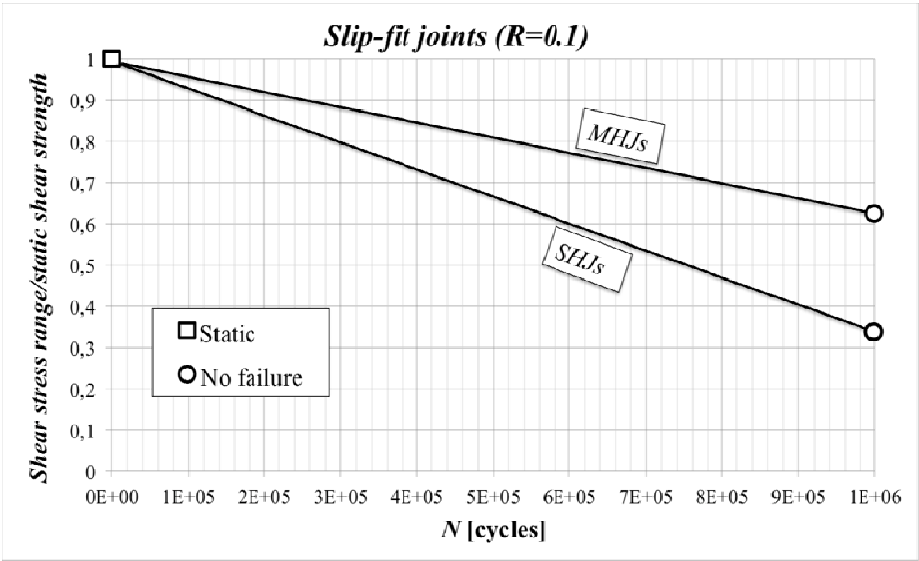


Figure 14. Comparison in  $\Delta\tau/\tau_{ad}$ - $N$ curves between *MHJs* and *SHJs* (stress ratio  $R=0.1$ ).

applicability (Figure 13) to press-fitted joints. Remembering that the interference contribution ( $F_{int} = \mu_A p_C A$ ) is constant with respect to fatigue, 3 joints were loaded as

$$\begin{cases} F_{\min} = 0.1 \cdot F_{\max} \\ F_{\max} = (\mu_A \cdot p_C + \Delta \tau_{\infty}) \cdot A = (\mu_A \cdot p_C + 0.62 \cdot \tau_{ad}) \cdot A \end{cases} \quad (9)$$

while other 3 joints as

$$\begin{cases} F_{\min} = 0.1 \cdot F_{\max} \\ F_{\max} = (\mu_A \cdot p_C + 0.8 \cdot \tau_{ad}) \cdot A \end{cases} \quad (10)$$

This test method was used because the coupling pressure cannot be exactly constant in all the tested specimens because of the tolerance differences in the interference values.

Specimens loaded by the fatigue cycle reported in Eq. (9) reached  $10^6$  cycles, without disengaging, whereas specimens stressed by the fatigue cycle reported in Eq. (10), beyond the expected fatigue limit, lasted between 350,000 and 550,000 cycles. The  $S-N$  curves reported in Figure 14 are, therefore, suitable also for the fatigue strength prediction of the adhesive contribution in press-fitted and adhesively bonded joints.

## 4. DISCUSSION

The anaerobic adhesive increases the joint performances both in *SHJs* and in *MHJs*. *MHJs* should be realized with steel shaft and aluminium hub, in presence of external load applied to the shaft: this is the way to bypass the aluminium compliance that modifies the actual interference both in tension and in compression. In press-fitted joints, by considering  $p_C$  within the 20-40 MPa range (standard coupling pressure values), the adhesive contribution in *SHJs* is higher than the interference contribution (up to 250% according to Figure 9a), whereas

the adhesive contribution in *MHJs* is lower than the interference contribution (about 40%, according to Figure9b); therefore, the effectiveness of anaerobic adhesive decreases in presence of the aluminium adherend (this occurrence is mainly due to the type of failure of the adhesive: cohesive -high strength- in *SHJs* vs adhesive -low strength- in *MHJs*). However, the same coupling pressure produces a similar total strength of the joint, since the friction coefficient in *MHJs* ( $\mu_A = 0.46$ ) is nearly 220% the one in *SHJs* ( $\mu_A = 0.21$ ). This occurrence is well shown in Figure15: in *SHJ* the adhesive is responsible for about 65% of the total strength (interference produces only 35%), while in the *MHJ* the percentages are swapped (interference 64%, adhesive 36%).

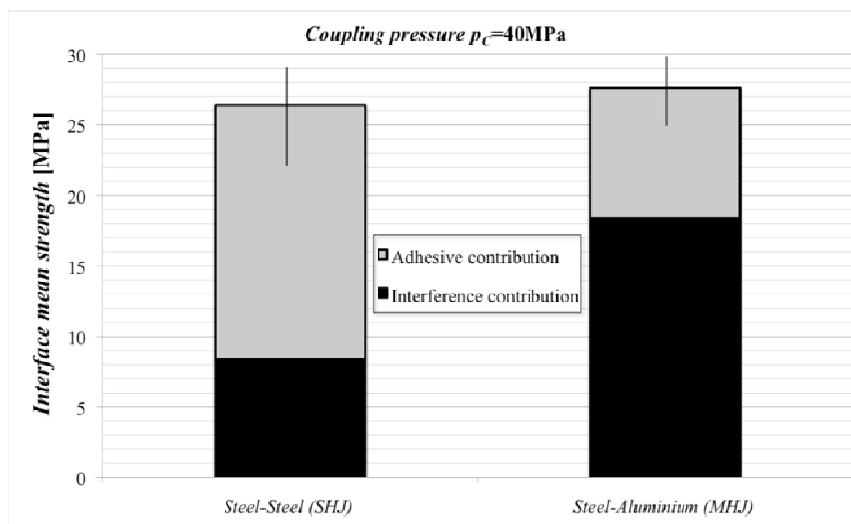


Figure 15. Comparison of total interface mean strength between *SHJ* [26] and *MHJ*: interference contribution ( $\mu_A \cdot p_C$ ) vs adhesive contribution ( $\tau_{ad}$ ).

$K_1$  and  $K_2$  are very useful coefficients to predict *MHJs* static strength and endurance limit, once the maximum coupling load is known (for instance derived by the load cell of the hydraulic press during the assembly phase).

Finally, the fatigue tests performed on *MHJs* (nearly pulsating tension,  $R = 0.1$ ) highlighted that in presence of a shear stress range equal to 62% of the static shear strength, the number of cycles equal to  $10^6$  can be reached, for both slip-fitted and press-fitted hybrid joints: in order to reach  $10^6$  cycles, the adhesive can be stressed up to 6 MPa, with a pulsating tension. In steel-steel press-fitted and

adhesively bonded joints the number of cycles equal to  $10^6$  can be reached again up to a shear stress of 6 MPa that is equal to 35% of the static shear strength ( $\tau_{ad} \approx 19$  MPa). Therefore, the value of 6 MPa, regardless of the adherend involved, seems to be the endurance limit for the anaerobic adhesive studied as well shown in Figure 16 ( $10^6$  cycles,  $R = 0.1$ , according to [31]). In brief, the adhesive static shear strength changes with the coupled materials (*SHJs* and *MHJs*) because of the change in the type of failure, whereas the adhesive endurance limit remains the same.

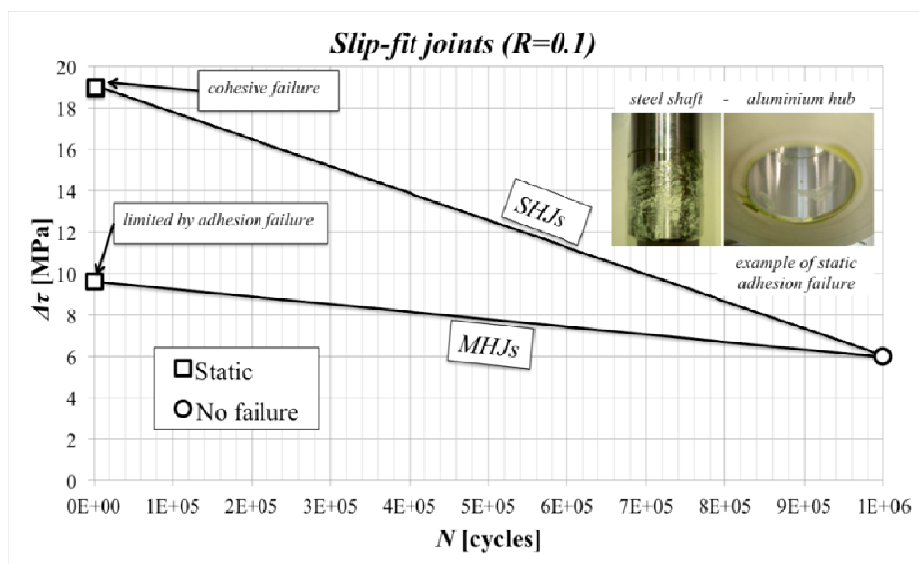


Figure 16. Comparison in  $\Delta\tau$ - $N$  curves between *MHJs* and *SHJs* (stress ratio  $R=0.1$ ).

## CONCLUSION

Static and fatigue strength properties of hybrid joints have been studied and reported in order to support designers in evaluating accurately the connection strength. Results derive from a collection of about 200 experimental tests performed by the Authors on a high strength, single-component adhesive, which cures anaerobically in contact with steel and/or aluminium. The adhesive contribution with respect to the total strength strictly depends on the adherend in contact: in presence of aluminium it is restricted by the weak bonding forces between aluminium and adhesive, leading to adhesion failures. However, if

coupling pressures of about 40 MPa (a standard value for interference-fit joints) are realized, steel-aluminium and steel-steel joints produce a similar total strength. In fact, the presence of higher friction coefficients is balanced by lower static adhesive strengths in steel-aluminium joints with respect to steel-steel ones. Furthermore, the endurance limit of mixed hybrid joints is also very close to that calculated for steel hybrid ones, at least within the analyzed ranges of pressure and in the presence of a high strength anaerobic adhesive.

## REFERENCES

- D. Croccolo, R. Cuppini and N. Vincenzi, in: *Proceedings of the 10<sup>th</sup> International Conference on the Science and Technology of Adhesion and Adhesives*, St. Catherine College, Oxford, UK, pp. 277-81 (2008).
- G. Bartolozzi, D. Croccolo and M. Chiapparini, *Öesterr. Ing. Z.5*, 198-201 (1999).
- E. Dragoni and P. Mauri, *Intl J. Adhesion Adhesives*20, 315-21 (2000).
- T. Sekercioglu, A. Gulsoz and H. Rende, *Mater. Design*26, 377-81 (2005).
- T. Sekercioglu, *Intl J. Adhesion Adhesives*25, 352-57 (2005).
- T. Sekercioglu and C. Meran, *Mater. Design*25, 171-75 (2004).
- T. Sekercioglu, H. Rende, A. Gulsoz and C. Meran, *J. Mater. Proc. Technol.*142, 82-86 (2003).
- R. Mengel, J. Haberle and M. Schlimmer, *Intl J. Adhesion Adhesives*27, 568-73 (2007).
- L. F. M. da Silva and R. D. Adams, *Intl J. Adhesion Adhesives*27, 362-79 (2007).
- R. D. Adams, J. Comyn and W. C. Wake, *Structural Adhesive Joints in Engineering*. Chapman & Hall, London (1997).
- H. Kawamura, T. Sawa, M. Yoneno and T. Nakamura, *Intl J. Adhesion Adhesives*23, 131-40 (2003).
- G. Romanos, *Intl J. Mater. Prod. Technol.*14, 430-43 (1999).
- D. Croccolo and R. Cuppini, *Intl J. Adhesion Adhesives*26, 490-97 (2006).
- D. Croccolo and R. Cuppini, *Intl J. Adhesion Adhesives*29, 280-85 (2009).
- S. Birch, *Automotive. Eng.*120, 8-12 (1994).
- JJ. Robinson, *J. Mater.*55, 6-10 (2003).
- D. Croccolo, M. De Agostinis and N. Vincenzi, *Eng. Failure. Anal.* 17,1173-87 (2010).
- LOCTITE Worldwide Design Handbook (1995).
- UNI EN10083, Steels for quenching and tempering - Part 3: Technical delivery conditions for alloy steels (2006).

- UNI EN 573, Aluminium and aluminium alloys - Chemical composition and form of wrought products - Part 1: Numerical designation system (2005).
- D. Croccolo, R. Cuppini and N. Vincenzi, *Strain*44, 170-79 (2008).
- G. Niemann, H. Winter and B. R. Hohn, *Maschinenelemente Bd I*, Springer-Verlag, Berlin (2005).
- D. Croccolo and N. Vincenzi, *Proc. Inst. Mech. Eng. C J. Mech. Eng. Sci.*223, 2231-39 (2009).
- DIN 7190, Interference fit – calculation and design rules (2001).
- NF E22-620, Assemblage frettes sur portee cylindrique, AFNOR, Paris la Defense (1984).
- D. Croccolo, M. De Agostinis and N. Vincenzi, *Intl J. Adhesion Adhesives*30, 359-66 (2010).
- UNI EN 20286, ISO system of limits and fits – Bases of tolerances, deviations and fits (1995).
- F. G. Kollmann, *Welle-Nabe Verbindungen*, Springer-Verlag, Berlin (1984).
- C. Borsellino, G. Di Bella and V. F. Ruisi, *Intl J. Adhesion Adhesives*29, 36-44 (2009).
- J. Comyn, *Intl J. Adhesion Adhesives*12, 45-49 (1992).
- ISO 9664, Adhesives – Test method for fatigue properties of structural adhesives in tensile shear (1993).
- D. Croccolo, M. De Agostinis and N. Vincenzi, *J. Adhesion Science and Technology*in press (2011).



## ***Chapter 6***

# **TISSUE ADHESIVES**

***Ankit Sarin, Govind Nandkumar and Gregory Dakin***

Department of Surgery, Weill Cornell Medical College,  
New York, NY, USA

## **INTRODUCTION**

The medical community has continually sought an efficient method of wound closure that requires little time and minimizes discomfort for patients, yet produces a good cosmetic outcome. Over the last few decades tissue adhesives have emerged as alternatives to traditional sutures and staples. These biological and synthetic compounds have the advantage of ease of use, excellent results, and high patient acceptability. In fact, the uses of these tissue adhesives have gradually evolved beyond wound closure to include a variety of medical applications as diverse as the treatment of cerebral arteriovenous malformations to the control of gastrointestinal bleeding. Tissue adhesives are an area of active research, with novel applications continuing to emerge.

This chapter summarizes the major types of adhesives available, tracing the history of development, and highlighting the unique properties of each of the five major compounds available: Cyanoacrylates, Albumin based compounds, Fibrin based & Collagen based adhesives, and Polyethylene Glycol Polymers. We also review the medical applications of these compounds as well as provide an overview of the major brands available in the US. We conclude with a brief discussion of the newer areas of research as well as emerging applications.

## CYANOACRYLATE GLUES

Cyanoacrylate is the generic name for cyanoacrylate-based fast-acting adhesives. Cyanoacrylates polymerize on contact with basic substances such as water or blood to form a strong bond.

Dr. Harry Coover and Fred Joyner of Kodak Laboratories invented cyanoacrylates in 1942 during experiments to make a transparent plastic suitable for gun sights. They found that 'their invention' would quickly bond together a variety of materials with great strength. Seeing possibilities for a new adhesive, Kodak developed "Eastman #910<sup>TM</sup>" a few years later as the first true "super glue."

This first adhesive was a methyl cyanoacrylate, which was studied extensively for its potential medical applications and was rejected due to its tissue toxicity, including inflammation and local foreign body reactions. N-butyl cyanoacrylate and Octyl cyanoacrylate were then brought into use and proved to be much more acceptable. In 1964, the Tennessee Eastman lab submitted its first application for drug approval to the FDA. The military learned of these new adhesives in 1966 and a special surgical team was flown to Vietnam, trained and equipped to use cyanoacrylate adhesives. A quick spray over the wounds stopped bleeding and bought time until conventional surgery could be performed. However the FDA never approved the drug.

N-butyl cyanoacrylate (as Histoacryl Blue<sup>TM</sup>) continued to be used extensively in Europe and Canada since the 1970s for a variety of surgical applications including middle ear surgery, bone and cartilage grafts, repair of cerebrospinal fluid leaks, and skin closure. In the US however, the FDA initially approved these products only for veterinary use: n-butyl- cyanoacrylate tissue adhesives Vetbond & Nexaband liquid and octyl-based Nexaband S/C (intended for topical skin closure when deep sutures had been placed) as adhesives suitable for use as suture alternatives. In 1998 however the FDA approved Dermabond<sup>TM</sup> (Octyl cyanoacrylate) for human use and since then several others have been approved. The different types of cyanoacrylates investigated are detailed below.

### Methyl 2-cyanoacrylate

Gaseous byproducts produced on heating it are strongly irritating to the lungs and eyes, which limits its potential applications.

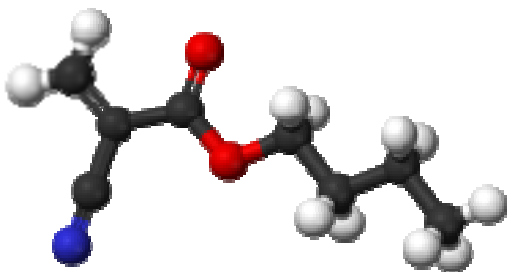
## ETHYL-2-CYANOACRYLATE

(Trade names: SuperGlue<sup>TM</sup>; Krazy Glue<sup>TM</sup>)

Ethyl cyanoacrylate is used for gluing various materials. Its application in medicine is limited because of the availability of less toxic alternatives n-butyl and octyl cyanoacrylates. Discussion of cyanoacrylates in this chapter will focus on these alternatives.

### N-butyl cyanoacrylate (and derivative isobutyl cyanoacrylate)

(Trade names: veterinary adhesives Vetbond<sup>TM</sup> and LiquiVet<sup>TM</sup>; and skin adhesives like Xoin<sup>TM</sup>, Indermil<sup>TM</sup>, LiquiBand<sup>TM</sup> and Histoacryl<sup>TM</sup>).

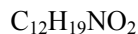
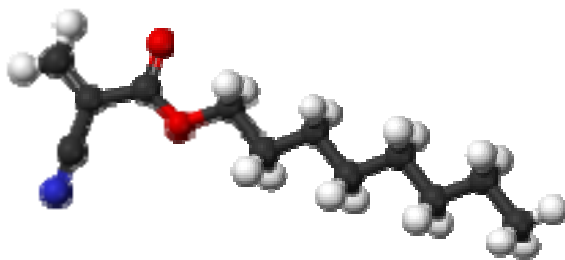


N-Butyl cyanoacrylate is a butyl ester of 2-cyano-2-propenoic acid. It is a clear colorless liquid with a sharp, irritating odor and is insoluble in water. It is soluble in acetone, methyl ethyl ketone, nitromethane, and methylene chloride.

N-Butyl cyanoacrylate (in monomer form) polymerizes rapidly in presence of ionic substances like moisture, blood or tissue fluids. The polymerized form has excellent tensile strength and is very effective in closing surgical or traumatic incisions making, it ideal for medical applications. In addition, the product inherently has some valuable bacteriostatic properties [1,2,3,4,5]. Also important is the manner of in-vivo degradation of polymerized butyl cyanoacrylate, which undergoes aqueous degradation resulting in byproducts whose concentrations are directly proportional to the rate of degradation, a function of the size of the polymerized molecule. This property of butyl cyanoacrylate has made it a very useful polymer to create various nano particles for delivery of drugs into the body with sustained release profiles.

## Octyl cyanoacrylate (and derivative 2-Octyl cyanoacrylate)

(Trade names: Derma+flex QS<sup>TM</sup>, SurgiSeal<sup>TM</sup>, FloraSeal<sup>TM</sup>, Dermabond<sup>TM</sup>, Surgi-Lock<sup>TM</sup> and Nexaband<sup>TM</sup>)



Octyl cyanoacrylate is an octyl ester of 2-cyano-2-propenoic acid. It is a clear colorless liquid with a sharp, irritating odor and like n-butyl cyanoacrylate, also polymerizes rapidly in the presence of moisture.

Butyl esters provide a stronger bond, but are quite rigid. Octyl esters, while providing weaker bonds, are more flexible. Heating these compounds to higher temperatures causes pyrolysis and depolymerization of the cured adhesive, which produces gaseous products strongly irritant to lungs and eyes.

## ALBUMIN BASED COMPOUNDS (GELATIN-RESORCINOL-FORMALDEHYDE GLUTARALDEHYDE GRFG GLUES)

This group of adhesives is based on the combination of albumin and adhesion compounds. The first-generation adhesives were true GRFG compounds containing gelatin, resorcinol, formaldehyde and glutaraldehyde. The second-generation compounds however are much less toxic, as the formaldehyde has been substituted with other cross-linking agents. These adhesives have greater bonding strength than fibrin based sealants and are less tissue reactive than cyanoacrylates. The only GRFG adhesive available in the United States is called BioGlue<sup>TM</sup> (CryoLife Inc., Kennesaw, GA), which is a combination of bovine albumin and glutaraldehyde glue. It has been primarily used in the repair of aortic dissections and sealing peripheral lung air leaks but we have shown that it has potential applications in reinforcing gastrointestinal anastomoses [6].

## **FIBRIN SEALANTS (NON-SYNTHETIC TISSUE ADHESIVES)**

Gelatin-resorcinol-formaldehyde and Cyanoacrylate adhesives can cause chronic inflammation and delay wound healing due to residual reaction products or degradation products such as glutaraldehyde and formaldehyde. Therefore, fibrin sealants that are based on the polymerization reaction between fibrinogen and thrombin have been widely used in clinical applications. However, they have low bonding strength to tissues and do not have the strength to bond skin. Two types of fibrin sealants are available on the market:

- 1) Purified thrombin promotes the conversion of the patient's own fibrinogen to fibrin;
- 2) A combination of a highly purified mixture of human fibrinogen, factor XIII and human thrombin solution [contains calcium and aprotinen (antifibrinolytic agent)].

These two components are then combined during administration to yield a fibrin clot.

In the United States, fibrin based adhesives are available from two commercial sources: Tisseel<sup>TM</sup> (Baxter, Westlake Village, CA) and Hemaseel<sup>TM</sup> (Hemacure, Sarasota, FL). In contrast to synthetic adhesives, fibrin sealants have the advantage of being biocompatible and biodegradable. The fibrin clot is resorbed within days to weeks as a part of the normal wound-healing process. As such, they are not associated with inflammation, foreign body reactions, tissue necrosis, or extensive fibrosis [7]. The disadvantage of fibrin products lies in the potential for infectious transmission especially of viruses since they are manufactured using plasma from pooled donors although the risk is extremely small.

## **COLLAGEN BASED ADHESIVES (NON-SYNTHETIC TISSUE ADHESIVES)**

Collagen-based adhesives represent a relatively new class of tissue adhesives. FloSeal<sup>TM</sup> (Sulzer Spine-tech, Anaheim, CA) and Proceed<sup>TM</sup> (Fusion Medical Technologies, Mountain View, CA) are chemically identical compounds: a combination of bovine thrombin and bovine collagen, which provides the matrix for the clot.

Another novel collagen product is CoStasis<sup>TM</sup> (Cohesion Technologies, Inc.,

Palo Alto, CA), which uses a combination of autologous human plasma obtained from patient's blood and a mixture of bovine collagen and thrombin.

## **HYDROGELS (POLYETHYLENE GLYCOL POLYMERS)**

Polyethylene glycol (PEG) polymers are hydrogels that are used for tissue adhesion. These adhesives are composed of photo reactive gelatins and a water-soluble dysfunctional macromer (cross-linking agent between the molecular chains of polymers). Photo reactive groups such as ultraviolet light-reactive benzophenone or visible light-reactive xanthene dyes (e.g., fluorescein sodium salt, Eosin Y, and Rose Bengal) are incorporated in the gelatins, which are then suspended in a saline solution containing polyethylene glycol diacrylate (PEGDA). This forms an adhesive hydrogel within one minute when irradiated with the appropriate light. The resulting gel bonds well to soft tissues such as the liver. This glue has great potential application in laparoscopic surgery, as the percutaneous delivery of the glue followed by in situ photogelation will result in prompt, safe and effective haemostasis [8]. FocalSeal-L™ (Genzyme Biosurgery, Inc., Cambridge, MA) is a water-soluble, bioabsorbable compound that requires a significant amount of time for photoactivation, thus limiting its use in hemostasis. However, another PEG polymer, CoSeal™ (Cohesion Technologies), does not require the same activation source and is currently being used in Europe for similar purposes.

## **MEDICAL APPLICATIONS OF THESE ADHESIVES**

### **Wound Closure**

Dermabond™ was the first FDA approved tissue adhesive in the US marketed to replace sutures that are 5-0 or smaller in diameter for incision or laceration repair. Several other compounds such as Histoacryl™, Surgiseal™ and Indermal™ are now also available. These adhesives have been shown to save time during wound repair, to provide a flexible water-resistant protective coating that in some cases is bacteriostatic, and to eliminate the need for suture removal. The long-term cosmetic outcomes are comparable to that of traditional methods of repair. Best suited for small, superficial lacerations, they may also be used on larger wounds where subcutaneous sutures have been employed. They are

relatively easy to use and patients, especially children, readily accept them over traditional methods of repair [9]. In addition, adhesives carry no risk of sharps injury.

#### **ADVANTAGES OVER SUTURES [10,11]**

- |                                                                                  |
|----------------------------------------------------------------------------------|
| - Maximum bonding strength at two and one-half minutes                           |
| - Equivalent in strength to healed tissue at seven days post repair              |
| - Less painful application, and sometimes no need for local anesthetic injection |
| - More rapid application and repair time                                         |
| - Cosmetically similar results at 12 months post-repair                          |
| - Better acceptance by some patients                                             |
| - Water-resistant covering                                                       |
| - Antimicrobial properties                                                       |
| - Does not require removal of sutures                                            |
| - Minimal training required for application                                      |
| - No risk of sharps injury                                                       |

It is absolutely essential that good wound management, including thorough irrigation and cleaning, be maintained prior to closure with tissue adhesives. In addition contraindications for adhesive use are listed in the table below.

#### **CONTRAINDICATIONS TO THE USE OF TOPICAL ADHESIVES [12,13,14]**

- |                                                                                                                                                                                                                                                                |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| - Jagged or stellate lacerations                                                                                                                                                                                                                               |
| - Bites, punctures or crush wounds                                                                                                                                                                                                                             |
| - Contaminated wounds                                                                                                                                                                                                                                          |
| - Mucosal surfaces                                                                                                                                                                                                                                             |
| - Axilla and perineum (high-moisture areas)                                                                                                                                                                                                                    |
| - Hands, feet and joints (unless kept dry and immobilized)                                                                                                                                                                                                     |
| - Patients with diabetes mellitus, chronic vascular disease, peripheral vascular disease, decubitus ulcers, prolonged steroid use, history of keloids, bleeding diathesis, allergy to adhesives (or formaldehyde), or any condition that delays wound healing. |

While no individual study has found a significant difference in complication rates between closure with tissue adhesives and standard sutured closure, pooling of data in the systematic review found a small but significant increased risk of wound dehiscence with use of tissue adhesives [15]. The same review, however, did find that application of tissue adhesives is significantly faster (average 5.7 minutes less) and less painful than standard wound closure.

## Closure of Surgical Incisions

The most comprehensive analysis comparing tissue adhesives to Standard closure of surgical incisions was by The Cochrane Review [16] that included 14 prior studies. The authors found that sutures were significantly better than tissue adhesives for minimizing dehiscence (10 trials). Sutures were also found to be significantly faster to use. For all other analyses of infection, patient and operator satisfaction and cost there was no significant difference between sutures and tissue adhesives. Notably, absent from the studies listed above were procedures involving incisions in areas of high tension (e.g., elbow and knee). Patients whose health status may have put them at high risk for impaired wound healing also were excluded from these studies. While tissue adhesives have not found favor in routine closure of surgical incisions, a retrospective chart review concluded that tissue adhesives could be used to close incisions from inguinal surgery in children in diapers [17]. More recently tissue adhesives have been shown to be useful in closure of laparoscopic port-site incisions [18].

## Gastrointestinal Applications

### *Gastric Variceal Bleeding*

Injection therapy with cyanoacrylates is now considered the first-line endoscopic intervention for bleeding gastric varices as well as secondary prevention of gastric variceal bleeds outside of the United States [19]. This technique has been shown to be more effective than band ligation in both hemostatic and rebleeding rates as well as need for blood transfusion [20]. Cyanoacrylates may also be superior to saline sclerotherapy for this purpose [21].

### *Esophageal Variceal Bleeding*

Cyanoacrylates are comparable to sclerotherapy in the endoscopic hemostasis of acute bleeds[22]. Comparison to band ligation in a randomized fashion has not been done. Fibrin sealants and Thrombin have also been evaluated for both esophageal and gastric variceal bleeding with marginal results primarily in the acute setting [23,24,25].

### *Peptic Ulcer Bleeding*

Cyanoacrylate injections are not as effective as suture / clips and cautery but are as effective as hypertonic saline for bleeding gastroduodenal ulcers, with the rebleeding rate being lower after cyanoacrylate injection [26]. Fibrin based

adhesives have also been shown to be effective in the treatment of bleeding gastroduodenal ulcers in a large randomized study, although multiple injections were required to show a benefit over polidocanol [27]. Compared with thermal devices and sclerosants, fibrin sealants may cause less tissue injury, and promote collagen deposition and ulcer healing, which is an attractive feature in the management of patients who require anticoagulation[28].

### ***Other Sources of GI Bleeding***

Cyanoacrylate injection has been used successfully in patients with Dieulafoy's lesions and bleeding tumors [29,30]. Fibrin adhesive injection has also been used in the endoscopic management of post-sphincterotomy bleeding and post-polypectomy bleeding [31,32]. CoStasis<sup>TM</sup>, which uses a combination of autologous human plasma and a mixture of bovine collagen & thrombin, has been successfully used for endoscopic control of severe upper gastrointestinal bleeding from metastatic cancer [33].

### ***Closure of Fistulous Tracts***

Endoscopic cyanoacrylate injections have been shown to be successful in the closure of pancreatic fistulas [34], biliary fistulas [35], and gastrointestinal fistulas [36]. There were relatively few complications in the studies quoted, although only a few well-selected patients were included. Only one randomized controlled trial has been performed for closure of entero-cutaneous fistulas, in which the fibrin-treated group was shown to have earlier closure of fistulas compared to controls [37]. Fibrin adhesive application has also been shown to be successful in the closure of anorectal fistulas [38] as well as tracheo-esophageal fistulas [39].

## **Cardiovascular and Haemostatic Applications**

Fibrin sealants and thrombin have been used extensively since the 1970s for hemostasis in cardiac surgery [40]. A number of newer alternatives such as CoStasis<sup>TM</sup> and FloSeal<sup>TM</sup> have also been marketed for surgical hemostasis. Fibrin glue is very effective in preventing bleeding from surface liver cracks that form during laparoscopic hepatic cryotherapy for in situ ablation of liver tumors. In addition to hemostasis, over the last 15 years or so, a number of new applications have emerged. Fibrin adhesives have been used for sealing of vascular grafts and treatment of aortic dissections [41]. Cyanoacrylates have been used to treat arteriovenous malformations by application of the compound into the abnormality through angiography [42]. More recently, BioGlue<sup>TM</sup> (combination of bovine

albumin and glutaraldehyde glue) has been used to fill the false lumen endovascularly in the repair of aortic dissections [43].

## Cerebrovascular Applications

N-Butyl cyanoacrylate has been used for embolization of cerebral arteriovenous malformations before their surgical treatment. Fibrin sealants have also been used in the management of cerebro-spinal fistulae [44]. Proceed<sup>TM</sup>, a collagen based tissue adhesive has been shown to have efficacy in the prevention and treatment of CSF leaks [45].

## Pulmonary Applications

FocalSeal<sup>TM</sup>, a polyethylene glycol polymer has been shown to decrease air leaks after major thoracic surgery [46]. Fibrin sealants have also shown efficacy in the treatment of broncho-pleural fistulas [47].

## TISSUE ADHESIVES AVAILABLE IN THE US

**VETBOND<sup>TM</sup>**: Manufactured by 3M and available for veterinary use it is an N-Butyl cyanoacrylate based adhesive.

**HISTOACRYL<sup>TM</sup>**: Manufactured by TissueSeal, it is a N-butyl cyanoacrylate adhesive available in either a translucent or blue (for better visualization) formulation. It was the first tissue adhesive on the market in Europe in the late 1970s and has since been used extensively for closure of topical skin wounds and small incisions.

**SURGISEAL<sup>TM</sup>**: Available from Adhezion Biomedical it is a 2-Octyl cyanoacrylate derived synthetic adhesive marketed for use to replace sutures that are 5-0 or smaller in diameter for incision or laceration repair.

**INDERMIL<sup>TM</sup>**: Available through Covidian, Indermil is a N-butyl cyanoacrylate tissue adhesive which remains liquid until exposed to water or water-containing substances / tissue, after which it cures (polymerizes) and forms a film that bonds to the underlying surfaces.

**BIOGLUE™**: Manufactured by Cryoglue, it has been available since 1998 and is composed of purified bovine serum albumin (BSA) and glutaraldehyde. The two glue components are dispensed by a controlled delivery system comprising a double-chambered syringe, applicator tips, and optional extender applicator tips. Once dispensed, the adhesive components are mixed within the applicator tip where the cross-linking begins. The glutaraldehyde molecules bond with the BSA molecules and, upon application to the tissue proteins at the repair site, create a flexible mechanical seal independent of the body's clotting mechanism.

BioGlue™ is indicated for use as an adjunct to standard methods of surgical repair (such as sutures, staples, electrocautery, and/or patches) to bond, seal, and/or reinforce soft tissue. BioGlue™ may also be applied alone to seal and/or reinforce damaged parenchyma when other ligature or conventional procedures are ineffective or impractical. Indicated soft tissues are cardiac, vascular, pulmonary, genitourinary, dural, alimentary (esophageal, gastrointestinal, and colorectal), and other abdominal tissues (pancreatic, splenic, hepatic, biliary). Additionally, BioGlue™ is used in the fixation of surgical meshes in hernia repair.

**TISSEEL™**: Marketed by Baxter, TISSEEL™ consists of a two-component fibrin sealant that offers concentrated human fibrinogen to stop diffuse bleeding in surgeries involving cardiopulmonary bypass (fully heparinized patients) and treatment of splenic injuries due to blunt or penetrating trauma to the abdomen, when control of bleeding by conventional surgical techniques, including suture, ligature, and cautery, is ineffective or impractical. It has also been used as an adjunct for sealing as well to prevent leakage from colonic anastomoses following the reversal of temporary colostomies. It is manufactured using processed, screened, pooled human plasma, (collected at US licensed collection centers), a vapor heating process, and a solvent detergent process. It is only intended for topical use as intravascular application of TISSEEL™ may result in life-threatening thromboembolic events.

**HEMASEEL™**: Manufactured by Haemacure Corporation its delivery and function is very similar to TISSEEL™.

**FLOSEAL™**: FloSeal™ Hemostatic Matrix consists of patented bovine-derived gelatin granules coated in human-derived thrombin that work in combination to form a stable clot at the bleeding site. Its advantages include its lack of need for refrigeration, relative ease of delivery to hard-to-reach surfaces and its ability to retain efficacy in wet, actively bleeding tissue unlike fibrin-based

products. It is marketed by Baxter.

**PROCEED<sup>TM</sup>**: Manufactured by Sulzer Medica and Fusion Medical Technologies Inc, Proceed<sup>TM</sup> Hemostatic Sealant was approved by the FDA in 1999. It is primarily indicated in neurological surgeries since there it has been shown to be more efficacious for hemostasis than the previous ‘gold standard’ Gelfoam and Thrombin.

**FOCALSEAL-L<sup>TM</sup>**: Marketed by Genzyme, FocalSeal-L<sup>TM</sup> surgical sealant was approved in 2000 for use as an adjunct to standard closure of visceral pleural air leaks incurred during elective pulmonary resection. It is, however, contraindicated for patients undergoing pneumonectomy or application over defects in bronchi, due to an increased incidence of bronchopleural fistulae observed in clinical studies. The FocalSeal-L<sup>TM</sup> Surgical Sealant system is comprised of synthetic absorbable sealant and primer solutions delivered to the target using two syringe applicators as liquids. On exposure of the photo-initiator, Eosin-Y in the solution to bluegreen light using a reusable source and a light wand, the primer and sealant solutions polymerize to form a crosslinked, clear, flexible, adherent hydrogel network.

**COSEAL<sup>TM</sup>**: Marketed by Cohesion Technologies, a unit of Baxter, CoSeal<sup>TM</sup> is a completely synthetic hemostatic sealing agent for use in vascular reconstructions to achieve adjunctive hemostasis by mechanically sealing areas of leakage. It does not need refrigeration and does not require any human blood products or bovine components to inhibit bleeding. However, this compound swells up to four times its volume within 24 hours of application, with additional swelling occurring as the gel resorbs. Therefore it should be applied only as a thin layer. Injecting directly into vessels is also contraindicated.

## NOVEL DIRECTIONS FOR RESEARCH

As mentioned earlier, GRF and cyanoacrylate based adhesives can cause chronic inflammation and delay wound healing due to the residual reaction products [48] or degradation products [49]. Fibrin adhesives have low cytotoxicity to the human body and promote wound healing, but their low bonding strength to tissues limits their use in medical field. In order to develop adhesives with low cytotoxicity and high bonding strength, some researchers have tried to use various crosslinking reagents including genipin [50], diepoxy compounds [51] and

carbodiimide [52]. These crosslinking reagents are reported to be much lower in cytotoxicity than aldehyde compounds [53]. N-hydroxysuccinimide (NHS) – poly (L-glutamic acid) esters were also reported to crosslink gelatin and adhere tissues with low cytotoxicity [54]. However, these adhesives have not yet had sufficient bonding strength or have had higher cytotoxicity.

## EMERGING APPLICATIONS

Given their unique properties and biocompatibility, new applications for the use of tissue adhesives continue to emerge. In one study [55] investigators have shown that BioGlue™ can reinforce both intact and defective stapled gastrojejunal anastomoses with demonstrated functional improvement *ex vivo*. While additional *in vivo* studies are warranted to determine whether it can prevent or help seal gastrojejunal leaks, if shown to do so, tissue adhesives could become increasingly used to reinforce gastrointestinal anastomosis preventing the catastrophic complications of leakage.

Similarly, other authors have shown that tissue adhesives could support sutures in minimally invasive endoscopic surgery [56].

Unusual applications include the use of tissue adhesives to fix peripheral nerve catheters [57] as well as the use of adhesives to fix mesh in inguinal hernia surgery [58].

Tissue adhesives could conceivably be engineered for slow, localized release of pain medications, antibiotics, chemotherapy, growth factors, and actual cell lines [59].

## REFERENCES

- Toriumi DM, Raslan WF, Friedman M, Tardy ME. Histotoxicity of cyanoacrylate tissue adhesives. *Arch Otolaryngol Head Neck Surg* 1990;116:546-50.
- Toriumi DM, Raslan WF, Friedman M, Tardy ME Jr. Variable histotoxicity of histoacryl when used in a subcutaneous site. *Laryngoscope* 1991;101:339-43.
- Quinn J, Maw J, Ramotar K, Wenckebach G, Wells G. Octylcyanoacrylate tissue adhesive wound repair versus suture wound repair in a contaminated wound model. *Surgery* 1997;122:69-72.

- Eiferman RA, Snyder JW. Antibacterial effect of cyanoacrylate glue. *Arch Ophthalmol* 1983;101: 958-60.
- Howell JM, Bresnahan KA, Stair TO, Dhindsa HS, Edwards BA. Comparison of effects of suture and cyanoacrylate tissue adhesive on bacterial counts in contaminated lacerations. *Antimicrob Agents Chemother* 1995;39:559-60.
- Nandakumar G, Richards BG, Trencheva K, Dakin G: Surgical adhesive increases burst pressure and seals leaks in stapled gastrojejunostomy. *Surg Obes Relat Dis.* 2010 Sep-Oct;6(5):498-501. Epub 2010 Jan 1.
- Spotnitz WD, Prabhu R: Fibrin sealant tissue adhesive: review and update. *J Long Term Eff Med Implants* 15:245-270, 2005.
- Cuschirri A, Crosthwaite G, Shimi S et al. *Surg endosc* 1995;9:483-9.
- Bruns, TB, Worthington, JM. Using tissue adhesive for wound repair: a practical guide to dermabond. *Am Fam Physician* 2000; 61:1383.
- Pearson, AS, Wolford, RW. Management of skin trauma. *Prim Care* 2000; 27:475.
- Toriumi, DM, Bagal, AA. Cyanoacrylate tissue adhesives for skin closure in the outpatient setting. *Otolaryngol Clin North Am* 2002; 35:103.
- Bernard, L, Doyle, J, Friedlander, SF, et al. A prospective comparison of octyl cyanoacrylate tissue adhesive (dermabond) and suture for the closure of excisional wounds in children and adolescents. *Arch Dermatol* 2001; 137:1177.
- Bruns, TB, Simon, HK, McLario, DJ, et al. Laceration repair using a tissue adhesive in a children's emergency department. *Pediatrics* 1996; 98:673.
- Edmonson, MB. Foreign body reactions to dermabond. *Am J Emerg Med* 2001; 19:240.
- Farion, K, Osmond, MH, Hartling, L, et al. Tissue adhesives for traumatic lacerations in children and adults. *Cochrane Database Syst Rev* 2002; CD003326.
- Coulthard P, Esposito M, Worthington HV, van der Elst M, van Waes OJ F, Darcey J. Tissue adhesives for closure of surgical incisions. *Cochrane Database of Systematic Reviews* 2010, Issue 5. Art. No.: CD004287.
- Ferlise, VJ, Ankem, MK, Barone, JG. Use of cyanoacrylate tissue adhesive under a diaper. *BJU Int* 2001; 87:672.
- Matin, SF. Prospective randomized trial of skin adhesive versus sutures for closure of 217 laparoscopic port-site incisions. *J Am Coll Surg* 2003; 196:845.
- Ryan BM, Stockbrugger RW, Ryan JM: A pathophysiologic, gastroenterologic, and radiologic approach to the management of gastric varices. *Gastroenterology* 126:1175-1189, 2004

- Lo GH, Lai KH, Cheng JS, et al: A prospective randomized trial of butyl cyanoacrylate injection versus band ligation in the management of bleeding gastric varices. *Hepatology* 33:1060-1064, 2001
- Akahoshi T, Hashizume M, Shimabukuro R, et al: Long-term results of endoscopic Histoacryl injection sclerotherapy for gastric variceal bleeding: a 10-year experience. *Surgery* 131:S176-S181, 2002
- Maluf-Filho F, Sakai P, Ishioka S, et al: Endoscopic sclerosis versus cyanoacrylate endoscopic injection for the first episode of variceal bleeding: a prospective, controlled, and randomized study in Child- Pugh class C patients. *Endoscopy* 33:421-427, 2001
- Datta D, Vlavianos P, Alisa A, et al: Use of fibrin glue (Beriplast) in the management of bleeding gastric varices. *Endoscopy* 35:675-678, 2003
- Heneghan MA, Byrne A, Harrison PM: An open pilot study of the effects of a human fibrin glue for endoscopic treatment of patients with acute bleeding from gastric varices. *Gastrointest Endosc* 56:422-426, 2002
- Kitano S, Hashizume M, Yamaga H, et al: Human thrombin plus 5 percent ethanolamine oleate injected to sclerose oesophageal varices: a prospective randomized trial. *Br J Surg* 76:715-718, 1989
- Lee KJ, Kim JH, Hahm KB, et al: Randomized trial of N-butyl-2-cyanoacrylate compared with injection of hypertonic saline-epinephrine in the endoscopic treatment of bleeding peptic ulcers. *Endoscopy* 32:505- 511, 2000
- Rutgeerts P, Rauws E, Wara P, et al: Randomised trial of single and repeated fibrin glue compared with injection of polidocanol in treatment of bleeding peptic ulcer. *Lancet* 350:692-696, 1997
- Laine L: Endoscopic therapy for bleeding ulcers: room for improvement? [editorial]? *Gastrointest Endosc* 57:557-560, 2003
- Yoshida T, Adachi K, Tanioka Y, et al: Dieulafoy's lesion of the esophagus correctly diagnosed and successfully treated by the endoscopic injection of N-butyl-2-cyanoacrylate. *Endoscopy* 36:183-185, 2004
- Rosa A, Sequeira C, Macas F, et al: Histoacryl in the endoscopic treatment of severe arterial tumor bleeding. *Endoscopy* 32:S69, 2000
- Born P, Ott R, Rosch T: Endoscopic hemostasis using fibrin sealant for post-sphincterotomy bleeding. Report of two cases. *Gastrointest Endosc* 51:731-733, 2000
- Venezia P: Drug targets in colonoscopic polypectomy: biological sealants with special reference to fibrin-glue (tissucol). *Curr Drug Targets Immune Endocr Metabol Disord* 5:339-345, 2005

- Milkes DE, Friedland S, Lin OS: A novel method to control severe upper GI bleeding from metastatic cancer with a hemostatic sealant: the CoStasis surgical hemostat. *Gastrointest Endosc* 55:735-740, 2002
- Seewald S, Brand B, Omar S, et al: Endoscopic sealing of pancreatic fistula by using N-butyl-2-cyanoacrylate. *Gastrointest Endosc* 59:463-470, 2004
- Seewald S, Groth S, Sriram PV, et al: Endoscopic treatment of biliary leakage with n-butyl-2 cyanoacrylate. *Gastrointest Endosc* 56:916-919, 2002
- Lee YC, Na HG, Suh JH, et al: Three cases of fistulae arising from gastrointestinal tract treated with endoscopic injection of histoacryl. *Endoscopy* 33:184-186, 2001
- Hwang TL, Chen MF: Randomized trial of fibrin tissue glue for low output enterocutaneous fistula. *Br J Surg* 83:112, 1996
- Sentovich SM: Fibrin glue for anal fistulas: long-term results. *Dis Colon Rectum* 46:498-502, 2003
- Willems IE, Dudley NE, Tam PKH: Endoscopic treatment of recurrent tracheo-oesophageal fistulae: long-term results. *Pediatr Surg Int* 13:256-258, 1998
- Borst HG, Haverich A, Walterbush G, et al: Fibrin adhesive: an important hemostatic adjunct in cardiovascular operations. *J Thorac Cardiovasc Surg* 84:548-553, 1982
- Sequin JR, Pricard E, Fapier J-M, et al: Aortic value repair with fibrin glue for type A acute aortic dissection. *Ann Thorac Surg* 58:304-307, 1994
- Lee BB, Do YS, Yakes W, Kim DI, Mattassi R, Hyon WS (March 2004). "Management of arteriovenous malformations: a multidisciplinary approach". *J. Vasc. Surg.* 39 (3): 590–600
- Reece TB, Maxey TS, Kron IL: A prospectus on tissue adhesives. *Am J Surg* 182:40S-44S, 2001
- Gnjidic Z, Tomac D, Negovetic L, et al: Fibrin sealant in the management of cerebrospinal fistulae. *Biomed Prog* 7:39-42, 1994
- Reece TB, Maxey TS, Kron IL: A prospectus on tissue adhesives. *Am J Surg* 182:40S-44S, 2001
- Reece TB, Maxey TS, Kron IL: A prospectus on tissue adhesives. *Am J Surg* 182:40S-44S, 2001
- Bouritzén C, Dromer M, Keinecke H-O: The effect of fibrin glueing to seal bronchial and alveolar leakages after pulmonary resections and decortications. *Eur J Cardiothorac Surg* 7:75-80, 1993
- Vanwachem PB, Vanluym MJA, Damink L, Dijkstra PJ, Feijen J, Nieuwenhuis P, *J. Biomed. Mater. Res.*, 1994, 28, 353.
- Tseng YC, Tabata Y, Hyon SH, Ikada Y, *J. Biomed. Mater. Res.*, 1990, 24, 1355.
- Sung HW, Huang DM, et al: *J. Biomed. Mater. Res.*, 1999, 46, 520.

- Nishi C, Nakajima N, Ikada Y, *J. Biomed. Mater. Res.*, 1995, 29, 829.
- Sekine T, Nakamura T, et al: *J. Biomed. Mater. Res.*, 2001, 54, 305.
- Sung SW, Huang RN, et al: *J. Biomater. Sci. Polym. Ed.*, 1999, 10, 63.
- Iwata H, Matsuda S, et al: *Biomaterials*, 1998, 19, 1869.
- Nandakumar G, Richards BG, Trencheva K, Dakin G: Surgical adhesive increases burst pressure and seals leaks in stapled gastrojejunostomy. *Surg Obes Relat Dis*. 2010 Sep-Oct;6(5):498-501. Epub 2010 Jan 1.
- Kjaergard HK: Suture support: is it advantageous? *Am J Surg* 182:15S-20S, 2001
- Klein, SM, Nielsen, KC, Buckenmaier CC, 3rd, et al. 2-octyl cyanoacrylate glue for the fixation of continuous peripheral nerve catheters. *Anesthesiology* 2003; 98:590.
- Negro P et al: Open tension-free Lichtenstein repair of inguinal hernia: use of fibrin glue versus sutures for mesh fixation. *Hernia*. 2011 Feb;15(1):7-14. Epub 2010 Jul 30
- Reece TB, Maxey TS, Kron IL: A prospectus on tissue adhesives. *Am J Surg* 182:40S-44S, 2001



# INDEX

## A

acetone, 16, 50, 139  
 acid, 82, 139, 140  
 acrylate, 52, 59  
 activation energy, 80  
 acute aortic dissection, 152  
 adhesion, viii, ix, 16, 42, 47, 48, 50, 53, 54,  
     55, 56, 57, 58, 59, 60, 62, 64, 65, 66, 67,  
     73, 74, 75, 82, 84, 95, 97, 98, 99, 102, 109,  
     124, 133, 140, 142  
 adhesion force, 73, 98  
 adhesion properties, 48  
 adhesions, 98  
 adhesive joints, 42, 43  
 adhesive materials, 41, 53, 62, 92  
 adhesive properties, 65, 101  
 adhesive strength, viii, 71, 80, 84, 115, 118,  
     127, 134  
 adolescents, 150  
 adsorption, 56, 97  
 adults, 150  
 aerospace, viii, 71, 74, 80  
 AFM, 99  
 albumin, 140, 146  
 allergy, 143  
 aluminium, ix, 6, 10, 16, 23, 24, 26, 42, 43,  
     113, 114, 115, 118, 119, 120, 121, 122,  
     123, 124, 125, 127, 129, 130, 131, 133, 135  
 amine, 75, 78, 80, 81

amine hardeners, 78  
 amplitude, 36  
 anastomosis, 149  
 anchorage, 73  
 angiography, 145  
 anorectal fistula, 145  
 anticoagulation, 145  
 antiviral agents, 67  
 Arrhenius equation, 80  
 arteriovenous malformation, x, 137, 145, 146,  
     152  
 asymmetry, 98  
 atmosphere, 103  
 atoms, 56, 100  
 Austria, 105  
 automotive application, 16, 17, 40  
 automotive applications, 16, 17, 40

## B

bacteriostatic, 139, 142  
 base, 32, 41, 48, 49, 55, 82  
 bending, 22  
 benefits, ix, 113, 114  
 binding energies, 105  
 biocompatibility, 149  
 bleeding, 138, 143, 144, 145, 147, 148, 151,  
     152  
 blood, 138, 139, 142, 144, 148  
 blood transfusion, 144

bonding, 2, 18, 44, 48, 55, 56, 57, 64, 66, 102, 114, 133, 140, 141, 143, 148  
 bonds, 82, 99, 102, 103, 140, 142, 146  
 bone, 17, 18, 138

## C

calcium, 141  
 candidates, 96  
 carbon, viii, 64, 66, 71, 72, 73, 74, 75, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 99, 107, 110, 111  
 carbon nanotubes, viii, 71, 73, 79, 88, 91  
 carboxyl, 68  
 cardiac surgery, 145  
 cardiopulmonary bypass, 147  
 cartilage, 138  
 cell line, 149  
 cell lines, 149  
 cerebrospinal fluid, 138  
 chain molecules, 98  
 challenges, 50  
 chemical, 17, 51, 56, 72, 73, 75, 80, 82, 84, 98, 99, 100, 102, 107, 109  
 chemical bonds, 51  
 chemical stability, 109  
 chemical vapor deposition, 107  
 chemicals, 61, 64  
 chemisorption, 98, 102, 103  
 chemotherapy, 149  
 children, 143, 144, 150  
 chloroform, 75, 76, 84  
 clarity, 60  
 classes, 49  
 classification, 69  
 cleaning, 14, 24, 62, 143  
 cleavage, 3  
 clinical application, 141  
 closure, ix, 137, 138, 143, 144, 145, 146, 148, 150  
 clustering, 102  
 coatings, 42, 55, 107  
 collagen, 141, 145, 146  
 color, 67  
 commercial, 72, 91, 109, 141

community, ix, 137  
 compatibility, 60, 82  
 compliance, 5, 87, 131  
 complications, 50, 145, 149  
 composites, 41, 43, 76, 77, 79, 81, 82, 85, 89  
 composition, 52, 65, 67, 99, 100, 135  
 compounds, ix, x, 51, 137, 140, 141, 142, 148  
 compression, 4, 27, 28, 29, 40, 41, 122, 131  
 condensation, 103  
 conduction, 50  
 conductivity, 66, 72, 73, 90  
 conductor, 72, 73, 80, 88  
 conductors, 74  
 configuration, 4  
 connectivity, 91  
 construction, 65, 66  
 contamination, 61, 82, 84, 97  
 cooling, 17, 55, 60, 96  
 copolymers, 48, 67  
 copper, 72, 118  
 correlation, 23, 25, 39  
 cosmetic, ix, 137, 142  
 cost, ix, 2, 22, 50, 61, 82, 95, 144  
 covalent bond, 59, 103  
 covering, 143  
 cracks, 4, 145  
 critical value, 72  
 cryotherapy, 145  
 CSF, 146  
 cure, 58, 82  
 cures, ix, 97, 113, 115, 133, 146  
 curing process, 18  
 CVD, 107  
 cycles, 36, 129, 131, 132  
 cytotoxicity, 148

## D

database, vii, 2, 41  
 decoupling, 119, 122, 123  
 decubitus ulcer, 143  
 defects, 4, 9, 17, 23, 40, 84, 109, 148  
 deficiencies, 51  
 deficiency, 49

- deformation, 3, 17, 20, 21, 23, 28, 29, 36, 37, 38, 39, 41, 42, 43, 57, 79, 86
- degradation, 61, 62, 108, 139, 141, 148
- dehiscence, 144
- depolymerization, 140
- deposition, 100, 101, 102, 103, 110, 145
- depth, 99
- designers, 133
- deviation, 120, 124, 126
- DGEBA, 78, 79
- diabetes, 143
- dielectric strength, 65
- differential scanning, 80
- differential scanning calorimetry, 80
- diffusion, 56, 115
- diglycidyl ether of bisphenol, 78
- discomfort, ix, 137
- dispersion, viii, 55, 66, 71, 74, 75, 76, 77, 80, 83, 90, 91, 100
- displacement, 5, 14, 17, 20, 21, 23, 32, 33, 34, 35, 36, 37, 39, 126
- distribution, vii, 1, 4, 5, 6, 7, 8, 10, 21, 25, 40, 43, 51, 66
- donors, 141
- dosage, viii, 47
- dressings, 67
- drug delivery, 67
- drugs, 139
- drying, 16, 50, 61, 62, 65
- dualism, 100
- ductility, 17
- durability, 42
- dusts, 119
- dyes, 142
- electron, 99, 100, 102
- electron cyclotron resonance, 100
- electronic circuits, viii, 47
- electrons, 82, 99
- elongation, 65
- emboli, 146
- embolization, 146
- embossing, 102, 108, 110
- emergency, 150
- emission, 61
- endurance, 132, 133, 134
- energy, 5, 55, 67, 79, 82, 84, 87, 88, 99, 100, 107, 115
- energy consumption, 88
- energy density, 100
- England, 41
- environment, 103, 107
- environmental impact, 50, 61
- epinephrine, 151
- epoxy resins, 90
- equilibrium, 100
- equipment, viii, 47, 52, 61, 62, 67
- esophagus, 151
- ester, 139, 140
- etching, 100
- ethyl acetate, 50
- ethylene, 48, 68
- ethylene oxide, 68
- Europe, 138, 142, 146
- evaporation, 55, 60, 84
- evolution, 30, 37, 43
- experimental condition, 75
- exploitation, 61
- exposure, 97, 148

|          |          |
|----------|----------|
| <b>E</b> | <b>F</b> |
|----------|----------|

- ECM, 87
- elastic deformation, 55, 120
- electric field, 101
- electrical conductivity, viii, ix, 66, 71, 72, 73, 89, 90, 91
- electrical properties, 64, 66, 72, 77
- electrocautery, 147
- electrodes, viii, 47

- fabrication, ix, 95, 96, 97
- Fabrication, 98
- FDA, 138, 142, 148
- fiber, viii, 71, 74, 81, 82, 83, 84, 85, 86, 87, 90
- fibers, 74, 79
- fibrillation, 88
- fibrin, 140, 141, 145, 147, 151, 152, 153

fibrinogen, 141, 147  
 fibrosis, 141  
 filled polymers, 90  
 fillers, 72, 73, 79  
 film formation, 50  
 film thickness, 108  
 films, viii, 47, 56, 60, 62, 64, 100, 101, 102, 110  
 filters, 67  
 finite element method, 5  
 fistulas, 145, 146, 152  
 fixation, 147, 153  
 flex, 140  
 flexibility, 79  
 fluid, 53  
 fluorine, 99, 102, 108  
 foils, 64  
 force, 54, 55, 57, 96, 97, 114, 115, 118, 120, 122, 123, 125, 126, 127, 128  
 formaldehyde, 140, 141, 143  
 formation, 57, 58, 59, 72, 74, 76, 85, 100, 102, 104  
 formula, 99  
 France, 1, 5, 44  
 free energy, 82, 84, 103  
 free volume, 80  
 friction, 99, 100, 107, 114, 115, 117, 119, 120, 132, 134  
 functionalization, 75, 89  
 fungus, 64

## G

gamma radiation, 68  
 gastrointestinal bleeding, x, 137, 145  
 gastrointestinal tract, 152  
 gastrojejunostomy, 150, 153  
 gel, 142, 148  
 geometrical parameters, 20, 22, 40, 116  
 geometry, ix, 3, 5, 6, 7, 8, 9, 10, 11, 12, 14, 15, 24, 25, 40, 42, 43, 54, 113  
 Germany, 68, 69, 105  
 glass transition, 48, 80, 96  
 glass transition temperature, 48, 80, 96  
 glasses, 67

glue, 138, 140, 142, 145, 147, 150, 151, 152, 153  
 glutamic acid, 149  
 glycol, 142, 146  
 granules, 147  
 graphite, 43  
 grounding, 67  
 growth, 88, 100, 125, 149  
 growth factor, 149

## H

haemostasis, 142  
 hardener, 75  
 hardness, 107, 119  
 hazards, 51  
 healing, 141, 145, 148  
 health, 144  
 health status, 144  
 height, 98  
 hemostasis, 142, 144, 145, 148, 151  
 hernia, 147  
 hernia repair, 147  
 heterogeneity, 5  
 hexane, 50, 103  
 high strength, ix, 113, 115, 132, 133  
 history, ix, x, 36, 37, 38, 95, 137, 143  
 homopolymers, 48  
 hub, 114, 115, 116, 117, 118, 119, 120, 122, 124, 131  
 human, 67, 138, 141, 142, 145, 147, 148, 151  
 human body, 67, 148  
 humidity, 50, 65, 67  
 hybrid, 114, 132, 133  
 hydrogels, 142  
 hydrophobic properties, 99  
 hydrostatic stress, vii, 2, 3, 29, 44  
 hydroxyl, 68, 103  
 hydroxyl groups, 68, 103  
 hypertonic saline, 144, 151  
 hypothesis, 14

**I**

ideal, 118, 139  
 identification, 27  
 image, 23, 25, 39, 48, 105  
 imprinting, 105, 107  
 improvements, 4, 74, 79  
 impurities, 105  
 in vivo, 149  
 incidence, 148  
 industries, viii, 55, 58, 64, 71  
 industry, 60, 65, 74, 80, 82, 115  
 infection, 144  
 inflammation, 138, 141, 148  
 ingredients, 61  
 inguinal, 144, 149, 153  
 inguinal hernia, 149, 153  
 initiation, 3, 4, 14, 38, 40, 44  
 injections, 144, 145  
 injuries, 147  
 injury, 143, 145  
 insulation, 65  
 insulators, 72, 81  
 integration, 30, 31  
 integrity, 91  
 interface, 5, 7, 8, 9, 14, 15, 21, 33, 39, 40, 43, 44, 55, 56, 57, 73, 75, 76, 88, 125, 126, 132  
 interference, vii, ix, 113, 114, 115, 116, 117, 118, 119, 120, 122, 124, 125, 126, 131, 132, 134  
 interphase, 18  
 intervention, 144  
 invariants, vii, 2, 3, 29  
 inversion, 32  
 ions, 82, 101  
 irrigation, 143  
 issues, 122  
 Italy, 113  
 iteration, 31

**J**

joints, vii, viii, 1, 3, 4, 5, 11, 12, 15, 16, 18, 23, 24, 34, 40, 41, 42, 43, 44, 71, 74, 81,

84, 86, 87, 88, 114, 115, 116, 120, 121, 122, 124, 125, 126, 129, 130, 131, 132, 134, 143

**L**

laceration, 142, 146  
 lack of confidence, 2  
 lead, 4, 6, 11, 20, 38, 65, 66  
 leakage, 147, 148, 149, 152  
 leaks, 138, 140, 146, 148, 149, 150, 153  
 lesions, 145  
 lifetime, 97  
 light, ix, 55, 72, 117, 127, 142, 148  
 liquid interfaces, 124  
 liquid phase, 55, 102, 103  
 liquids, 51, 84, 148  
 lithography, vii, ix, 95, 96, 97, 98, 100, 102, 107, 109, 110, 111  
 liver, 142, 145  
 local anesthetic, 143  
 lumen, 146

**M**

magnitude, 72, 89  
 management, 143, 145, 146, 150, 151, 152  
 manufacturing, viii, 48, 51, 65, 67, 71, 74, 82, 92, 96  
 masking, 60, 63  
 mass, 57, 108  
 materials, 2, 3, 5, 36, 47, 48, 66, 67, 73, 74, 81, 82, 88, 91, 92, 98, 108, 115, 117, 119, 120, 133, 138, 139  
 matrix, 17, 32, 64, 72, 75, 76, 78, 82, 86, 90, 99, 141  
 matrixes, 75  
 matter, 56, 115, 120  
 measurement, 17, 19, 39, 56, 99, 101, 108  
 measurements, 43, 99  
 mechanical properties, ix, 3, 5, 10, 18, 42, 60, 72, 73, 75, 78, 79, 87  
 media, 49, 50  
 medical, ix, x, 60, 61, 67, 137, 138, 139, 148

medicine, 139  
 melt, 51, 55, 60, 61, 62, 65  
 melts, 51  
 metals, 42, 64, 72, 100, 118, 119  
 metastatic cancer, 145, 152  
 meter, 107  
 methodology, 115  
 methylene chloride, 139  
 micrometer, 79, 102  
 microstructures, 110  
 military, 138  
 mixing, 75, 76  
 modelling, 32, 33, 44  
 models, vii, 1, 4, 18, 29, 32, 33, 41, 43, 56  
 modulus, 5, 6, 10, 17, 40, 42, 78, 79, 114, 116, 117  
 moisture, 64, 67, 139, 140, 143  
 mold, ix, 95, 97, 98, 99, 100, 102, 103, 104, 105, 106, 107, 108, 109  
 molds, 107  
 molecular weight, 49, 51, 52, 82  
 molecules, 49, 56, 58, 59, 98, 100, 102, 103, 147  
 monolayer, 102, 103, 104  
 monomers, 49, 52, 58, 59  
 morphology, 82, 99  
 multiplier, 30

## N

nanocomposites, 74, 75, 77, 78, 79, 87, 89, 91  
 nanofibers, viii, 71, 73, 79, 82, 84, 86, 91  
 nanoimprint, vii, ix, 95, 96, 97, 98, 100, 102, 107, 108, 110, 111  
 nanometer, 96, 103  
 nanometer scale, 96  
 nanometers, 107  
 nanoscale structures, 97  
 nanotube, 74, 87  
 necrosis, 141  
 nerve, 149, 153  
 NH<sub>2</sub>, 78  
 nickel, 66, 67, 72, 98, 100, 101, 102  
 nitrogen, 103  
 noble metals, 91

nodes, 96  
 numerical analysis, 19, 20, 21  
 numerical tool, 2

## O

oesophageal, 151  
 OH, 103  
 oligomers, 52  
 operations, 119, 121, 152  
 opportunities, 51  
 optical micrographs, 75, 76  
 optimization, viii, 2, 42, 74  
 organic solvents, 49, 50  
 overlap, 3, 6, 7, 8, 9, 10, 11, 12, 13, 20, 21, 27, 40  
 overlay, 97  
 oxygen, 115, 118

## P

pain, 149  
 parallel, 43, 97, 118  
 parenchyma, 147  
 particle bombardment, 100  
 particle morphology, 50  
 peptic ulcer, 151  
 percolation, 72, 73, 89, 90  
 percolation theory, 72  
 perineum, 143  
 peripheral vascular disease, 143  
 permit, 48, 50, 67  
 pH, 65  
 pharmaceutical, viii, 47, 67  
 physical and mechanical properties, 72  
 physical properties, 57  
 pilot study, 151  
 plasticity, 30, 41, 45  
 plasticizer, 51  
 plastics, 42, 61, 62, 67  
 PM, 151  
 PMMA, 102  
 pneumonectomy, 148  
 Poland, 47

polar, 14, 61, 62, 67, 82, 84  
 polar groups, 82  
 polarity, 50  
 polycarbonate, 67  
 polyesters, 48, 52  
 polyether, 48, 52  
 polymer, 48, 50, 51, 52, 57, 60, 72, 75, 82, 90,  
   96, 97, 100, 101, 102, 139, 142, 146  
 polymer chain, 51, 75  
 polymer chains, 51, 75  
 polymer films, 100  
 polymer matrix, 72, 82  
 polymer structure, 52  
 polymeric materials, 60, 100  
 polymerization, 48, 49, 50, 75, 100, 103, 110,  
   141  
 polymerization process, 48, 49, 50, 100  
 polymerization processes, 48, 49  
 polymers, 41, 48, 49, 50, 51, 58, 72, 100, 110,  
   118, 142  
 polypectomy, 145, 151  
 polypropylene, 67  
 polyurethanes, 48, 67  
 preparation, 16  
 prevention, 144, 146  
 probe, 54  
 process innovation, 50  
 propagation, 85, 87, 88  
 protection, 107  
 protective coating, 142  
 proteins, 147  
 PTFE, 99, 100, 101, 102, 108  
 PVC, 58, 59, 65  
 pyrolysis, 140

## Q

quality control, 55  
 quartz, 98, 105, 106, 107  
 quasi-static loading, 17

## R

radiation, 66

radical polymerization, 49  
 radio, 82, 101  
 radius, 6  
 raw materials, 48, 49  
 reactions, 138, 141, 150  
 reactive groups, 142  
 reagents, 148  
 recovery, 43  
 reinforcement, 87  
 relaxation, viii, 2, 36, 38, 41, 43, 58  
 relief, 96  
 repair, 138, 140, 142, 143, 146, 147, 149, 150,  
   152, 153  
 replication, 96, 110  
 reproduction, 108  
 requirements, 49, 50, 53, 64, 65, 91, 107  
 researchers, 82, 148  
 resection, 148  
 resins, 61, 67, 84  
 resistance, 42, 50, 51, 57, 58, 60, 61, 62, 64,  
   65, 66, 67, 72, 73, 107, 109  
 resolution, ix, 77, 88, 95, 96  
 resorcinol, 140, 141  
 response, vii, 2, 18, 23, 32, 34, 35, 38  
 RIE, 96, 107  
 risk, 16, 141, 143, 144  
 room temperature, 48, 51, 52, 68, 80, 96, 103  
 root, 30  
 rotations, 23  
 roughness, 82, 84, 99, 114, 115, 117, 119, 120  
 rubber, 42, 67, 79  
 rubbers, 61, 65  
 rules, 15, 29, 41, 135

## S

scanning electron microscopy, 77, 85  
 scatter, 4, 17, 19, 21, 23, 28, 40, 125  
 science, viii, 41, 47  
 sclerosis, 151  
 sclerotherapy, 144, 151  
 SEM micrographs, 86, 106  
 sensitivity, 4, 54  
 serum, 147  
 serum albumin, 147

- shape, 17, 66, 72, 74, 98  
 shear, vii, ix, 1, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12,  
     13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23,  
     24, 25, 26, 27, 28, 29, 32, 33, 34, 35, 36,  
     37, 38, 39, 40, 41, 42, 43, 44, 53, 57, 58,  
     65, 66, 72, 74, 75, 76, 84, 85, 86, 96, 114,  
     124, 125, 129, 132, 135  
 shear deformation, 27  
 shear strength, ix, 53, 57, 65, 66, 72, 74, 84,  
     85, 86, 114, 124, 125, 129, 132  
 showing, 76, 88  
 silane, 102, 103  
 silica, 102, 103, 104  
 silicon, 98, 102  
 silicones, 48, 67  
 silver, 66, 72, 91  
 simulation, 41  
 simulations, 5  
 SiO<sub>2</sub>, 102, 107  
 SiO<sub>2</sub> surface, 102  
 skin, 67, 68, 138, 139, 141, 146, 150  
 sodium, 142  
 solid state, 53  
 solubility, 60, 65  
 solution, 14, 55, 103, 141, 142, 148  
 solvents, 49, 50, 61, 103  
 Spain, 71  
 species, 82, 101  
 specific surface, 66, 80  
 spectroscopy, 99  
 stability, 66, 72, 107, 109  
 stabilization, 50  
 stabilizers, 50  
 standard deviation, 87, 120, 124, 126  
 state, vii, 1, 2, 4, 10, 11, 14, 15, 19, 20, 22, 23,  
     25, 27, 30, 31, 40, 41, 48, 51, 53, 56, 99  
 steel, ix, 5, 6, 8, 9, 10, 14, 15, 16, 26, 29, 34,  
     44, 67, 113, 115, 117, 118, 120, 121, 122,  
     123, 124, 125, 127, 129, 130, 131, 132, 133  
 sterile, 67  
 stress, vii, ix, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11,  
     12, 13, 14, 15, 18, 19, 20, 21, 22, 23, 24,  
     25, 26, 27, 28, 29, 30, 31, 33, 38, 40, 41,  
     43, 44, 57, 58, 59, 66, 74, 79, 113, 115,  
     116, 129, 130, 132, 133  
 stress concentrators, 74  
 stress intensity factor, 44  
 structure, 11, 14, 48, 56, 73, 81, 90, 91, 100,  
     101, 102, 105  
 structuring, 100  
 substitution, 115  
 substrate, 4, 6, 7, 8, 9, 10, 11, 13, 14, 15, 16,  
     21, 39, 40, 53, 55, 59, 62, 64, 66, 74, 82,  
     96, 97, 98, 101, 102, 103, 105, 107  
 substrates, 3, 5, 6, 8, 10, 14, 15, 16, 18, 19,  
     20, 21, 23, 24, 25, 26, 29, 34, 53, 61, 88,  
     100  
 Sun, 74, 92  
 supplier, 66  
 suppliers, viii, 47  
 surface area, 73, 79, 82, 90  
 surface energy, 82, 84, 99, 101, 103, 107, 108,  
     124  
 surface layer, 82  
 surface properties, 50, 82  
 surface tension, 83, 84  
 surface treatment, 82, 84  
 surfactant, 62  
 surgical technique, 147  
 suture, 138, 142, 144, 147, 149, 150  
 swelling, 148  
 Switzerland, 1  
 synthesis, 49, 68, 75, 100  
 synthetic rubbers, 48

|          |
|----------|
| <b>T</b> |
|----------|

- target, 100, 101, 148  
 techniques, 3, 19, 27, 39, 40, 50, 75, 90, 101,  
     109, 114  
 technologies, 97  
 technology, 41, 48, 50, 52, 69, 96, 97, 109  
 teflon, 100, 110  
 telephone, 65  
 temperature, ix, 41, 43, 51, 59, 65, 66, 72, 75,  
     80, 96, 102, 108, 115, 117  
 tensile strength, 44, 139  
 tension, 3, 4, 42, 55, 84, 120, 122, 129, 131,  
     132, 144, 153  
 testing, 2, 5, 17, 23, 34, 36, 39, 54, 58, 115

textiles, 68  
 texture, 82  
 therapy, 144, 151  
 thermal properties, 65, 74, 91  
 thermal resistance, 73  
 thermal stability, 99  
 thermal treatment, 75, 77  
 thin films, 99, 101  
 thrombin, 141, 142, 145, 147, 151  
 tissue, vii, ix, 67, 84, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 149, 150, 152, 153  
 titanium, 67, 118  
 toluene, 50  
 torsion, 4, 24  
 toxicity, 138  
 toys, viii, 47  
 training, 143  
 transition temperature, 48  
 transmission, 67, 141  
 transparency, 97  
 transpiration, 67  
 trauma, 147, 150  
 treatment, ix, x, 16, 56, 72, 75, 76, 80, 82, 84, 97, 100, 109, 137, 145, 146, 147, 151, 152  
 trial, 31, 145, 150, 151, 152  
 tumor, 151  
 tumors, 145

## U

UK, 134  
 ulcer, 145  
 ultrasound, 75  
 uniform, 91, 103  
 United States (USA), 43, 45, 69, 92, 137, 140, 141, 144  
 UV, 51, 52, 65, 68, 69, 96, 105, 107, 108, 111  
 UV irradiation, 52  
 UV light, 97

## V

vacuum, 100  
 valence, 56  
 vapor, ix, 67, 95, 96, 100, 102, 103, 147  
 vapor phase deposition, ix, 95, 96, 103  
 variations, 9, 115  
 vector, 5, 43  
 vehicles, 115  
 versatility, 48, 49  
 vessels, 148  
 Vietnam, 138  
 viruses, 141  
 visco-elastic properties, 50, 51, 57  
 viscosity, viii, 51, 52, 68, 71, 74, 80, 91, 96  
 visualization, 146

## W

water, 48, 50, 51, 60, 61, 62, 65, 73, 99, 103, 105, 107, 108, 138, 139, 142, 146  
 water absorption, 73  
 wear, 99, 107, 109, 120  
 web, 51, 60, 61  
 wettability, 54, 80, 81, 84, 91, 124  
 wetting, 50, 51, 53, 54, 55, 82, 84, 99, 103  
 wood, 64  
 wound dehiscence, 143  
 wound healing, 141, 143, 144, 148

## X

XPS, 99, 101, 105, 106, 108

## Y

yield, vii, 2, 29, 30, 31, 41, 141